

Physical Chemistry Part 2

CHAPTER 1

Solid State

1.1–1.86

<i>Overview</i>	<i>1.1</i>
1.1 Introduction	1.5
1.2 General Characteristics of Solid State	1.5
1.3 Classification of Solids	1.5
1.3.1 Crystalline Solids	1.5
1.3.2 Amorphous Solids	1.5
1.4 Classification of Crystalline Solids	1.6
1.4.1 Molecular Solids	1.6
1.4.2 Metallic Solids	1.6
1.4.3 Covalent or Network Solids	1.7
1.4.4 Ionic Solids	1.7
1.5 Types of Symmetry in Crystals	1.8
1.6 X-ray Study of Crystals	1.10
1.7 Lattice	1.11
1.7.1 Five Types of Two-Dimensional Lattices	1.12
1.8 Crystal Lattices and Unit Cells (3D)	1.13
1.8.1 Primitive and Centred Unit Cells	1.13
1.8.2 Seven Crystal System	1.14
1.9 Effective Number of Atoms (Z_{eff}) in a Unit Cell	1.16
1.10 Atomic Radius and Shortest Distances in Cubic System	1.23
1.11 Coordination Number (CN)	1.24
1.12 Packing Fraction (PF) or Space Occupied by Atoms in a Cubic System	1.25
1.13 Calculation of the Density of a Metal by Using Unit Cell Dimensions	1.26
1.14 Close-packed Structures	1.28
1.14.1 Coordinate Number (CN) of hcp and ccp Structures	1.31
1.14.2 Relationship Between Formula of a Compound and Number of Voids Filled	1.31
1.14.3 Stacking Sequence	1.32

1.14.4	Location of Tetrahedral and Octahedral Voids	1.32
1.15	Structure of Ionic Crystals	1.35
1.15.1	Radius Ratio Rules	1.35
1.15.2	Coordination Number in Some Ionic Compounds	1.38
1.16	Structures of Simple Ionic Compounds	1.38
1.16.1	Simple Ionic Compounds of Type AB	1.38
1.16.2	Simple Ionic Compounds of Type AB ₂ (Fluorite Type)	1.40
1.16.3	Simple Ionic Compounds of Type A ₂ B (Antifluorite Type)	1.40
1.16.4	Relation Between Edge Length a and Radius of Cation and Anion in Ionic Compounds	1.41
1.17	Structure of Diamond	1.42
1.18	Spinel Structures	1.42
1.18.1	Normal Spinel Structures	1.42
1.18.2	Inverse Spinel Structures	1.42
1.19	Corundum Structure	1.43
1.19.1	Structure of the Oxides of Iron	1.43
1.20	Perovskite Structure	1.45
1.21	Rutile Structure	1.45
1.22	Calculation of Effective Atoms in an hcp Unit Cell	1.46
1.23	Effect of Temperature and Pressure on a Crystal Structure	1.47
1.24	Haüy's Law of Rational Indices	1.52
1.24.1	Weiss Indices	1.53
1.24.2	Miller Indices	1.53
1.24.3	d -Spacings	1.53
1.24.4	Interplanar Distances for Cubic System	1.53
	<i>Concept Application Exercise 1.1</i>	1.55
1.25	Polymorphism and Allotropy	1.56
1.25.1	Isomorphism and Isopolymorphism	1.57
1.26	Imperfections in Solids	1.57
1.26.1	Electronic Imperfections	1.58
1.26.2	Atomic or Point Defects	1.58
1.26.3	Line Defects or Dislocations	1.61
1.27	Electrical Properties of Solids	1.62
1.27.1	Conduction of Electricity in Metals	1.62
1.27.2	Conduction of Electricity in Semiconductors	1.63
1.27.3	Electron-Rich Impurities	1.63
1.27.4	Electron-Deficit Impurities	1.63
1.27.5	Applications of n -Type and p -Type Semiconductors	1.63
1.28	Magnetic Properties of Solids	1.63
1.28.1	Paramagnetism	1.64
1.28.2	Diamagnetism	1.64

1.28.3 Ferromagnetism	1.64
1.28.4 Antiferromagnetism	1.64
1.28.5 Ferrimagnetism	1.64
1.29 Dielectric Properties of Solids	1.65
1.29.1 Summarization of Dielectric Properties of Polar Crystals	1.65
<i>Concept Application Exercise 1.2</i>	1.66
<i>Exercises</i>	1.67
<i>Single Correct Answer Type</i>	1.67
<i>Multiple Correct Answers Type</i>	1.77
<i>Linked Comprehension Type</i>	1.81
<i>Matrix Match Type</i>	1.82
<i>Numerical Value Type</i>	1.83
<i>Archives</i>	1.84
<i>Answers Key</i>	1.86

1

Solid State

OVERVIEW

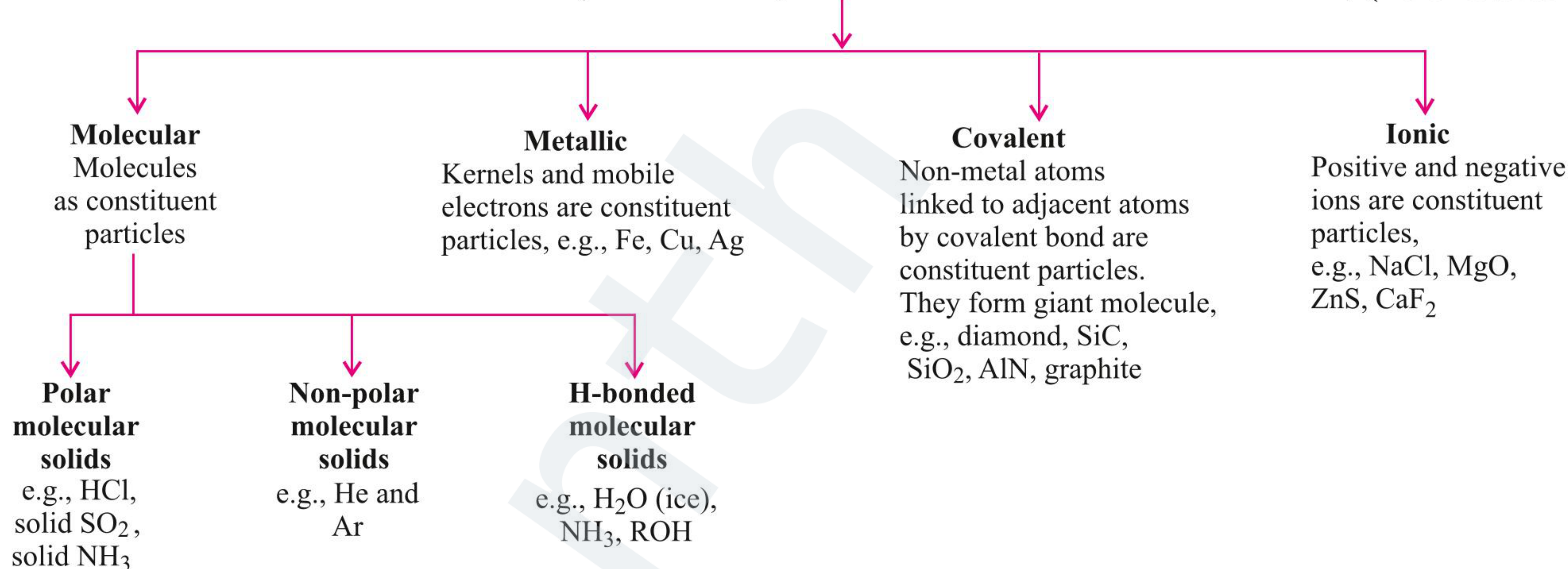
1. **Solid:** It is a form of matter which possesses rigidity and hence a definite shape and volume.

2. **Classification of solids (Refer to Table 1.1)**



Note: All elements and compounds (including alloys) are crystalline whereas rubber, glass, plastics, etc., are amorphous.

3. **Classification of crystalline solids (on the basis of intermolecular forces in them) (Refer to Section 1.4)**



4. **Types of symmetry in crystals**

a. **Law of symmetry:** It states that all crystals of a substance possess the same element of symmetry. Three important elements of symmetry are:

- i. Plane of symmetry
- ii. Axis of symmetry
- iii. Centre of symmetry.

b. The total number of elements of a symmetry in a cubic crystal = 23

- i. Plane of symmetry = 3 (rectangular plane of symmetry)
+ 6 (diagonal plane of symmetry)
= 9

- ii. Axis of symmetry = 3 (four-fold or a tetrad axis of symmetry)
+ 4 (three-fold or triad axis of symmetry)
+ 6 (two-fold or diad axis of symmetry) = 13

iii. Centre of symmetry or inversion of symmetry = 1
∴ Total number of elements of symmetry in a cubic crystals = 9 + 13 + 1 = 23

c. **Axis of six-fold or a hexad axis of symmetry:** This type of symmetry is possible in hexagonal crystals and not in cubic crystals.

5. **Crystal lattice and unit cells**

a. A crystal lattice is a 3-D arrangement of constituent particles in a crystal.

A unit cell is the smallest portion of a crystal lattice which when repeated in different directions gives the entire lattice.

Thus, for a 3-D lattice, a unit cell is described by three edges (a , b , and c) and angles between them (α , β , and γ).

b. **Seven crystal systems and 14 Bravais lattice:** Just as there are five possible 2-D lattices, there are seven crystal systems which constitute 14 possible 3-D lattices and are called Bravais lattices.

6. a. Close-packed structures in three dimensions:

Hexagonal close packing (hcp) is ABA–ABA... arrangement of layers in which tetrahedral voids (TVs) of second layer are covered by the spheres of third layer. This arrangement of atoms is found in metals such as Mg and Zn.

Cubic close packing (ccp) is ABC–ABC... arrangement of layers in which the third layer is placed above the second layer in a manner such that its spheres cover the octahedral voids (OVs). This is also called face-centred cubic (fcc) structure. Metals such as Cu and Ag crystallize in this structure.

- b. fcc or ccp and hcp are close packed arrangements in which the coordination number is 12, 74% space is occupied, and 26% is empty while bcc is not a close packed arrangement and has a coordination number of 8, 68% space occupied, and 32% is empty.
7. a. Number of atoms present in a close packed structure = Number of octahedral voids = 4 per unit cell
- b. Number of TVs = $2 \times \text{OVs} = 2 \times \text{Number of atoms in a close packed structure} = 8/\text{unit cell}$
- c. Number of TVs = $2 \times \text{Number of occupied voids}$
- d. Number of atoms (or ions) present in a close packed structure (fcc or ccp) = 4/unit cell

$$\text{Number of TVs} = 8/\text{unit cell} = \frac{8}{4} = 2/\text{atom}$$

$$\text{Number of OVs} = 4/\text{unit cell} = \frac{4}{4} = 1/\text{atom.}$$

8. Radius of TV = $0.225r$

$$\text{Radius of OV} = 0.414r$$

where r is the radius of ions (mostly cations) in the packing.

9. Location of TVs and OVs in a close packed structure

(Refer to Section 1.14.4)

10. Radius ratio rule

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}} = \frac{r_{\oplus}}{r_{\ominus}} \text{ or } \frac{r_c}{r_a} \text{ or } \frac{r}{R}$$

11. Structures of ionic crystals

Ionic compounds have any one of the following three types of structures:

- a. **AB type:** Rock salt (NaCl) type, CsCl-type structure, zinc blende (Zns) or sphalerite-type structure.
- b. **AB₂ type:** Fluorite type, e.g., CaF₂, BaF₂, etc.
- c. **A₂B type:** Antifluorite type, e.g., Na₂O, Li₂O, etc.
- d. **Ligancy as a function of radius ratio in 1 : 1 or AB-type structure (Refer to Table 1.11)**

12. Hexagonal close packed structure (hcp)

- a. Z_{eff} in hcp = 6/unit cell = Number of OVs
Number of TVs = $6 \times 2 = 12/\text{unit cells}$
- b. Base area of hexagon = $6\sqrt{3}r^2$

$$\begin{aligned} \text{c. Height of hexagon (c)} &= 4r \times \sqrt{\frac{2}{3}} \\ &= 2a \times \sqrt{\frac{2}{3}} \quad (\because a = 2r) \end{aligned}$$

$$\text{d. Volume of unit cell of hexagon} = 24\sqrt{2}r^3$$

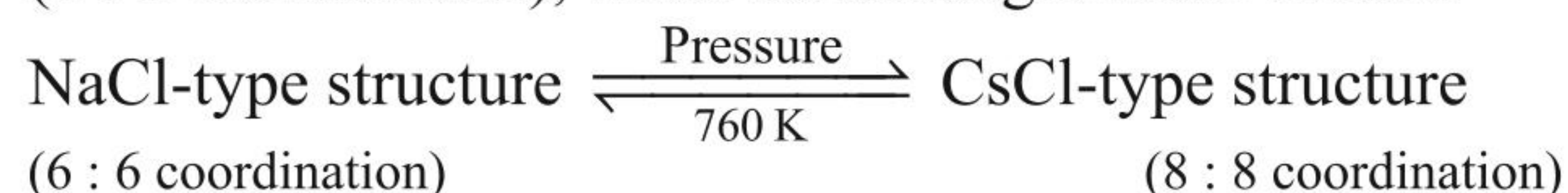
$$\begin{aligned} \text{e. Packing fraction} &= \frac{6 \times \text{Volume of atom}}{\text{Volume of unit cell}} \\ &= \frac{6 \times \frac{4}{3} \pi r^3}{24\sqrt{2}r^3} = \frac{\pi}{3\sqrt{2}} = 0.74 \end{aligned}$$

$$\text{f. } \frac{c}{a} \text{ ratio of ideally close packed hcp crystal:}$$

$$\frac{c}{a} = \frac{4r}{2r} \sqrt{\frac{2}{3}} = 2 \sqrt{\frac{2}{3}} = 1.633$$

13. Effect of temperature and pressure on the crystal structure

On the application of high pressure, NaCl-type structures (6 : 6 coordination) transform to CsCl-type structures (8 : 8 coordination), while on heating reverse occurs.

**14. Structure of diamond cubic (dc)**

(Refer to Section 1.17)

15. Normal spinel structures (AB₂O₄)

(Refer to Section 1.18.1)

16. Inverse spinel structure (AB₂O₄) type

(Refer to Section 1.18.2)

17. Corundum structure (A₂O₃ type)

(Refer to Section 1.19)

18. Structure of red brown α -Fe₂O₃

[Refer to Section 1.19.1(b)]

19. Structure of Fe₃O₄ ($\overset{\text{II}}{\text{FeO}} \cdot \overset{\text{III}}{\text{Fe}_2\text{O}_3}$ or $\overset{+2}{\text{FeO}} \cdot \overset{+3}{\text{Fe}_2\text{O}_3}$)

It has inverse spinel structure. [Refer to Section 1.19.1(d)]

20. Perovskite structure (BaTiO₃)

(Refer to Section 1.20)

21. Rutile structure (TiO₂)

(Refer to Section 1.21)

22. a. Void volume in ionic compound

Void volume per unit volume of unit cell

$$= 1 - \text{Packing fraction}$$

- b. Refer to Table 1.12 for summary of the main characteristics and examples of some simple ionic solids.

23. a. Law of rational indices (Hauy's law): Refer to Section 1.24.

- b. Weiss indices:** The coefficients of unit intercepts (a, b, c , i.e., l, m, n are known as Weiss indices of a plane. For example, for a crystal plane which cuts through the crystal axis at $(2a, 3b, c)$, the Weiss indices = 2, 3, 1.
- c. Miller indices:** Reciprocal of the Weiss coefficients and multiplying through by the smallest number that will express all the reciprocals as integers.

For example: Weiss indices = 2 3 1

$$\text{Reciprocal} = \frac{1}{2} \quad \frac{1}{3} \quad \frac{1}{1}$$

$$\text{Simplifying} = 3 \quad 2 \quad 6$$

Miller indices are (3 2 6).

- d. d -spacing:** The distance between two parallel planes in a cubic crystal is given by:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a = edge of the cube, and h, k , and l are Miller indices of the parallel plane.

- e. d -spacing for sc, fcc, and bcc**

$$\text{For sc: } d_{100} : d_{110} : d_{111} = a : \frac{a}{\sqrt{2}} : \frac{a}{\sqrt{3}}$$

$$\text{For fcc: } d_{200} : d_{220} : d_{111} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}}$$

$$\text{For bcc: } d_{200} : d_{110} : d_{222} = \frac{a}{2} : \frac{a}{\sqrt{2}} : \frac{a}{2\sqrt{3}}$$

- 24. a. Polymorphism:** The occurrence of different crystal forms of the same substance is called polymorphism. For example, ZnS (zinc blende) and ZnS (wurtzite).
- b. Allotropy:** Polymorphism occurring in elements is called allotropy. Allotropy can be of three types:
- Enantiotropy:** One form is interconvertible to another at a fixed transition temperature under specified pressure, e.g., at 96.6°C, rhombic S is converted to monoclinic S and vice versa.
 - Monotropy:** One form is unstable at all temperatures and is converted to stable form, e.g.,

$$\text{O}_2 \longrightarrow \text{O}_3, \text{ red P}_4 \longrightarrow \text{yellow P}_4.$$
 - Dynamic allotropy:** Both forms exist side by side in equilibrium at all temperatures, e.g., λ and μ sulphur.
- c. Isopolymorphism:** If each of the two different forms of a polymorphic substance is isomorphous with a form of another polymorphic substance, then it is called isopolymorphism.
- d. Law of isomorphism:** According to Mitscherlich, isomorphous substances have similar chemical constitution, i.e., they have the same number of atoms similarly arranged and therefore have same formula. For example, K_2SO_4 and K_2CrO_4 ; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ are isomorphous.

25. Imperfections in solids

- a.** Irregularities in the arrangement of constituent particles are called *defects*.
- b. Impurity defect:** This defect is due to the presence of foreign atoms at lattice sites (in place of host atoms)

or at vacant interstitial sites. For each Ba^{2+} or Sr^{2+} ion introduced into NaCl crystal one hole is created (one vacancy) which makes NaCl as a semi-conductor.

- c.** The number of Schottky defects present in an ionic crystal containing N ions at temperature T is given by:

$$n = Ne^{-E/2KT},$$

where E is the energy required to create these n Schottky defects and K is the Boltzmann constant and is equal to

$$= \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J K}^{-1}.$$

- d.** The number n of Frenkel defects in an ionic crystal containing N ions and N_i , the number of interstitial sites at a temperature T , is given by:

$$n = \left(\frac{N}{N_i} \right)^{\frac{1}{2}} e^{-E/2KT}$$

where E is the energy required to create n Frenkel defects.

For NaCl at 1000 K, the energies of formation of these defects are 2 eV and 3 eV, respectively (1 eV = 1.602×10^{-19} J).

- e.** Fraction of the surface of a crystal vacancy is given by:

$$\frac{n}{N} = e^{-E/RT}$$

- 26. a. Conduction of electricity in metals and semiconductors:** Metallic conductors conduct electricity due to the movement of electrons while electrolytes conduct electricity due to the movement of ions.

The conductivity of metals depends upon the number of valence electrons available per atom. These atomic orbitals of metal atoms form molecular orbital which are so close in energy to each other as to form a *band*.

In metals, there is no gap between valence band and conduction band. Hence, electrons can flow easily under an applied electric field and the metal shows conductivity.

In insulators, the gap between valence band and conduction band is large; electrons cannot jump to over it and such a substance has very low conductivity.

In semiconductors, the gap between valence and conduction band is small, hence some electrons may jump to conduction band and show some conductivity. Si and Ge show this type of behaviour and are called *intrinsic semiconductors*. The conductivity of a semiconductor increases with rise in temperature.

- b. Doping:** The conductivity of an intrinsic semiconductor increases by adding a suitable impurity. This process is called doping, and it can be done by adding an impurity which is electron rich or electron deficient as compared to Si or Ge. Such impurities introduce *electronic defects*.
- c. Electron-rich impurities (n -type semiconductor):** When Si (Group 14) is doped with phosphorous (Group 15), unshared electrons make Si n -type (negatively charged electron) semiconductor.

- d. Electron-deficient impurities (*p*-type semiconductor):** When Si (Group 14) is doped with aluminium (Group 13), holes are created and Si becomes *p*-type (positively charged holes) semiconductor.
- e. Diode:** It is a combination of *n*-type and *p*-type semiconductors and is used as a rectifier.
- f. Transistors:** They are made by sandwiching a layer of one type of semiconductor between two layers of other type of semiconductor. *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals.
- g. Group 13–15 compounds** are InSb, AlP, and GaAs. In, Al, Ga (Group 13) and Sb, P, As (Group 15) elements.
- h. Group 12–16 compounds** are ZnS, CdS, CdSe, and HgTe. Zn, Cd, Hg (Group 12) and S, Se, Te (Group 16) elements.
- 27. Magnetic properties:** Substances are classified into five categories on the basis of their magnetic properties:
- Diamagnetism:** Such substances are weakly repelled by a magnetic field. It is shown by those substances which have all paired electrons, e.g., H_2O , NaCl , and C_6H_6 . They are weakly magnetized in magnetic field in opposite direction.
 - Paramagnetism:** Such substances are weakly attracted by a magnetic field. It is shown by those substances which have one or more unpaired electrons. They are magnetized in magnetic field in the same direction, e.g., O_2 , Cu^{2+} , Fe^{3+} , Cr^{3+} . They lose their magnetism when magnetic field is removed.
 - Ferromagnetism:** Such substances remain permanently magnetized even when magnetic field is removed. For example, Fe, Co, Ni, and CrO_2 .
 - Antiferromagnetism:** Such substance have zero magnetic moment because there are equal number of electrons with opposite spin. For example, MnO .
 - Ferrimagnetism:** Such substances have small magnetic moment because they have unequal number of electrons with opposite spin. For example, Fe_3O_4 , MgFe_2O_4 , and ZnFe_2O_4 .
These substances also lose ferrimagnetism on heating and become paramagnetic.
 - Curie temperature:** The temperature above which no ferromagnetism is observed is known as curie temperature.
- 28. Dielectric properties or electrical properties of polar crystals:** Polar crystals are classified into five categories on the basis of their electrical properties.
- Piezoelectricity:** When mechanical stress is applied on a polar crystal, electricity is produced due to the displacement of ions. For example, PbZrO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, and quartz.
 - Pyroelectricity:** The electricity produced on heating a polar crystal is called pyroelectricity.
 - Ferroelectricity:** Ferroelectric crystals remain permanently polarized even in the absence of electric field. For example, BaTiO_3 , Rochelle Salt, KH_2PO_4 .
 - Antiferroelectricity:** Antiferroelectric crystals have net zero dipole moment because they have equal number of opposite dipoles. For example, PbZrO_3 .
- Note:** All ferroelectric crystals are piezoelectric but reverse is not true.
- Superconductivity:** When the electrical resistance of a substance becomes almost zero, it is called superconductor. For example, $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 90 K.
- Note:**
- Hg becomes superconductor at 4 K.
 - Amorphous silica is used in making photovoltaic cell (to convert sunlight into electricity).

1.1 INTRODUCTION

Matter can be classified into three categories depending upon its physical state, namely, solid, liquid, and gas.

1.2 GENERAL CHARACTERISTICS OF SOLID STATE

Under a given set of conditions of temperature and pressure, whether a substance will exist as a solid, liquid, or gas depends upon the net effect of two opposing factors:

- Intermolecular forces:** These forces exist among the constituent particles (atoms, molecules, or ions) and tend to keep the molecules closer.
- Thermal energy:** This energy among the constituent particles is due to temperature and tends to keep them apart by making them move faster.

At sufficiently low temperature, the thermal energy is low, but intermolecular forces are so strong that the particles come so close that they cling to one another and occupy fixed positions and are unable to move. They can still oscillate about their mean positions and the substance exists in solid state.

Some of the common characteristics of solids which distinguish them from the other two states of matter are:

- Solids have definite volume irrespective of the size or shape of the container in which they are placed.
- Solids are rigid and have definite shapes.
- Many solids have a crystalline appearance and have definite pattern of angles and planes.
- Solids are almost incompressible, having compressibility approximately 10^6 times more than gases.
- Solids have a much higher density (mass-to-volume ratio) than that of gases or liquids.
- Solids diffuse very slowly as compared to liquids or gases. Constituent particles are very closely packed in solids permitting very little space for their movement.
- Most solids become liquid when heated. Some undergo sublimation on heating. The temperature at which a solid changes into liquid is called *melting point* and the process is called as *melting*. Due to the varying nature of solids, their melting temperatures vary considerably.

1.3 CLASSIFICATION OF SOLIDS

On the basis of the nature of order present in the arrangement of their constituent particles, solids are classified as crystalline or amorphous.

1.3.1 CRYSTALLINE SOLIDS

All solid elements (metal and non-metals) and compounds exist in crystalline form. In a crystal, the arrangement of constituent particles is of long range order. It usually consists of a large number of small crystals each of which has the same regular pattern or arrangement of particles. This arrangement repeats itself periodically over the entire crystal.

Crystalline solids have a sharp (characteristic) melting point. They are anisotropic in nature, that is, they show different physical

properties such as refractive index, electrical resistance (or conductance), thermal expansion, etc., along different directions in the same crystal. This is due to different arrangement of particles in different directions, which results in the value of same physical property to be different along each direction, as shown in Fig. 1.1. NaCl and quartz are some examples of crystalline solids.

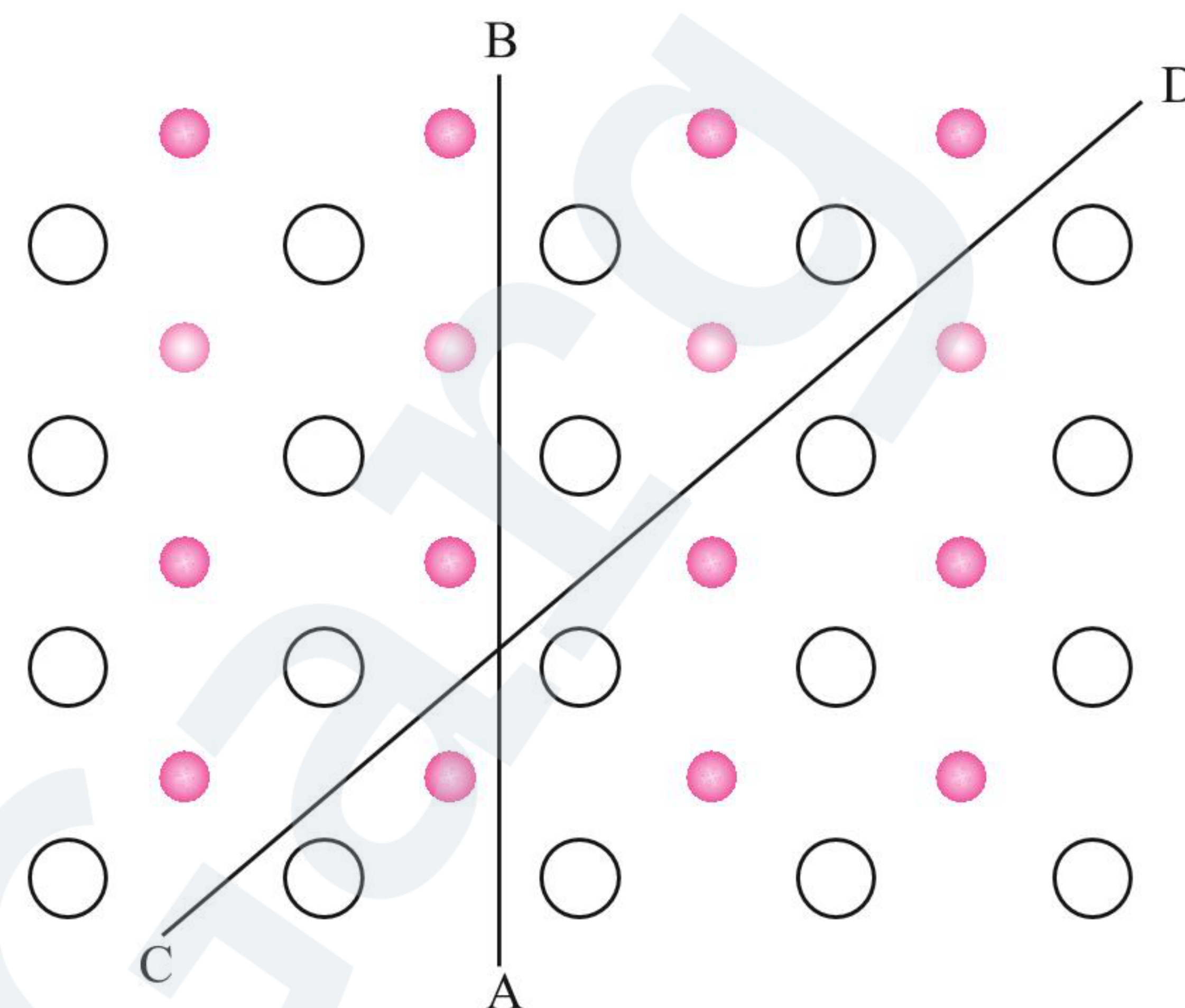


Fig. 1.1 Anisotropy in crystals due to different arrangement of particles along different directions

1.3.2 AMORPHOUS SOLIDS

In amorphous solid (Greek: *a* without; *morphe* 'shape, form'), the arrangement of constituent particles is of short range order and consists of particles of irregular shape. In such an arrangement, a regular and periodically repeating pattern is short distance only. Such portions are scattered and in between the arrangement is disordered. Crystalline solids are isotropic in nature because there is no long range order in them and the arrangement is irregular along all the direction. That is, they show similar physical properties (like, refractive index, electrical resistance or conductance, thermal expansion, etc.) along any direction.

The structures of quartz (crystalline) and quartz glass (amorphous), respectively, are almost identical. Yet in the case of amorphous quartz glass, there is no long range order, and its structure is similar to that of liquids. Glass, rubber, and plastics are some examples of amorphous solids.

In fact, only the crystalline solids are *true solids* whereas amorphous solids are considered to be highly supercooled liquids of very high viscosity and are called *pseudosolids*. Like liquids, amorphous solids have a tendency to flow slowly. This is supported by the fact that the glass panes fixed in the windows or doors of old buildings are found to be slightly thicker at the bottom than at the top. This is because glass flows down very slowly and makes the bottom portion slightly thick.

Moreover, due to short range order in amorphous compounds, small parts of an amorphous solid crystallizes while rest does not crystallize. This is also supported by the fact that some glass objects from ancient civilization are found to become milky in appearance because of crystallization.

The main points of distinction between crystalline and amorphous solids are summarized in Table 1.1.

Table 1.1 Distinction between crystalline and amorphous solids

	Properties	Crystalline solids	Amorphous solids
a.	Melting point	They have sharp melting points.	They do not have sharp melting points.
b.	Crystal geometry	The internal arrangement of particles is regular, so they possess definite and regular geometry. They have long range order.	The internal arrangement of particles is irregular. Thus, they do not have any definite geometry. They have short range order.
c.	Heat of fusion	They have characteristic heat of fusion.	They do not have characteristic heat of fusion.
d.	Physical state	Crystalline solids are hard and rigid, shape is not distorted by mild distorting forces.	Amorphous solids are comparatively soft and not very rigid. These can be distorted by bending or compressing forces.
e.	External form	There is regularity in the external form when crystals are formed. Crystalline solids give a regular cut when cut with a sharp-edged knife.	There is no regularity in the external form when amorphous solids are formed. Amorphous solids give irregular cut.
f.	Anisotropic or isotropic nature	Crystalline solids are anisotropic. This implies that physical properties such as refractive index, conductivity, thermal expansion, etc., are different in different directions. This is due to orderly arrangement of particles.	Amorphous solids are isotropic in nature. This implies that various physical properties are same in all the directions. This is because of the random arrangement of particles.
	Examples	Crystals of NaCl, CsBr, CaF ₂ , and ZnS.	Rubber, glass, and plastic.

Note: Some substances adopt different arrangements under different conditions. Such compounds are called as polymorphs. These different structures have different properties such as melting point, density, etc. For example, diamond and graphite are two different polymorphic forms of carbon.

1.4 CLASSIFICATION OF CRYSTALLINE SOLIDS

Most of the solid substances are crystalline, for example, metallic elements such as Fe, Ag, Au, Cu, and non-metallic elements such as phosphorous (P₄), sulphur (S₈), and I₂. Compounds such as NaCl, ZnS, and naphthalene form crystalline solids.

They are further classified on the basis of the nature of intermolecular forces in them into four types (a) molecular, (b) metallic, (c) covalent, and (d) ionic solids.

1.4.1 MOLECULAR SOLIDS

The constituent particles in molecular solids are molecules. They are further subdivided into the following types:

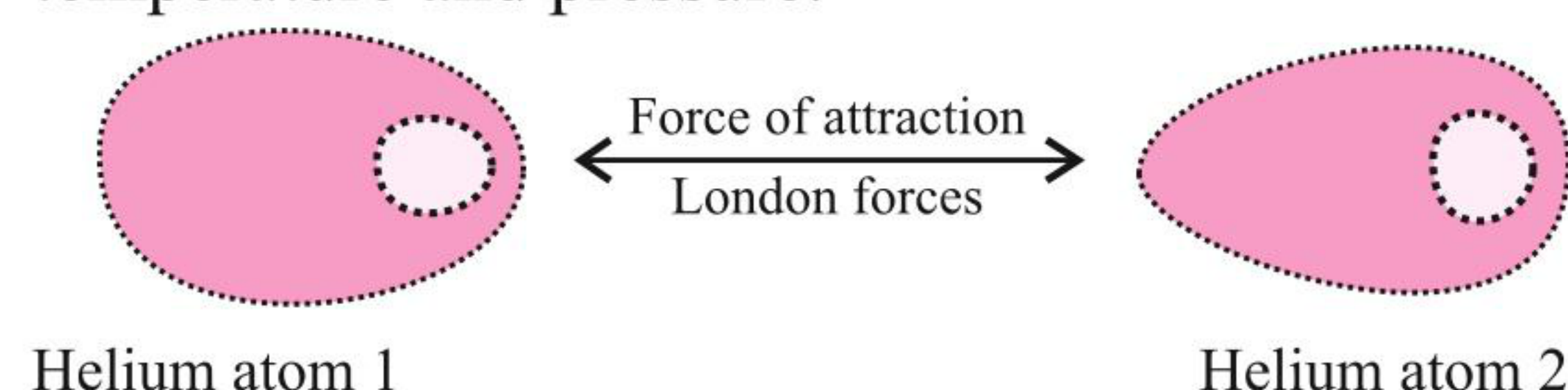
- a. Polar molecular solids:** They are formed by covalent bonds. The molecules are held by relatively stronger dipole–dipole interactions (Fig. 1.2). Their melting points are higher than those of non-polar molecular solids. These solids are soft and non-conductors of electricity. Some of them are gases or liquids under room temperature and pressure.

Example: HCl, solid SO₂, and solid NH₃.

**Fig. 1.2** Dipole–dipole force of attraction

- b. Non-polar molecular solids:** They are formed by either atoms (e.g., He and Ar) or molecules formed by non-polar covalent bonds (e.g., H₂, Cl₂, and I₂). The atoms or

molecules are held by weak dispersion forces or London forces (Fig. 1.3). Like polar molecular solids, they are also soft and non-conductors of electricity. But their melting points are lower than those of polar molecular solids. They are usually present in liquid or gaseous state at room temperature and pressure.

**Fig. 1.3** Weak London dispersion forces

- c. Hydrogen-bonded molecular solids:** In such solids, the molecules contain polar covalent bonds between H and F, O, or N atoms. Hence, the intermolecular forces of attraction in these molecules are the strong hydrogen bonds, e.g., H₂O (ice), NH₃, ROH, glycol (HOCH₂—CH₂OH), etc.

They are volatile liquids or soft solids at room temperature and pressure. They are non-conductors of electricity. Their melting and boiling points are generally higher than the molecular solids of the first two types.

1.4.2 METALLIC SOLIDS

In such solids, the constituent particles are orderly arranged positively charged metal ions (called *kernel*s) surrounded by a sea of free electrons. These electrons are mobile and are evenly spreaded out throughout the crystal and flow throughout the metal crystal such as water in the sea. These are produced from metal atoms having low ionization energy and can easily lose their valence electrons to leave behind positively charged ions (*kernel*s). Each metal atom contributes one or more electrons towards this sea of mobile electrons. Hence, it is called electron sea model.

Metallic bonding is also explained by *electron gas model* because the electrons are free to move in all directions like the molecules of a gas. These mobile electrons are simultaneously attracted by the positive ions (*kernels*) and hence hold these positive ions together. *The force that holds the metal ions together in the crystal is called metallic bond.* Greater the number of mobile electrons, greater is the force of attraction, and hence stronger is the metallic bonding resulting in high melting and boiling points.

Following are the characteristics properties of metallic solids:

- a. They possess high electrical and thermal conductivity. When an electrical field is applied, the mobile electrons flow through the network of positive ions. Similarly, when heat is supplied to one portion of the metal, the thermal energy is uniformly spreaded throughout by free electrons.

- b. They possess lusture and colour in certain cases. This is also due to the presence of free electrons in them.

When visible light falls on the metal, the free electrons oscillate about their mean position and reflect light in all directions and thus are lustrous.

- c. They are highly malleable and ductile. This is because of the non-directional nature of the metallic bonding. On beating, one layer of metal slides over the other because the position of the positive ions can be altered without destroying the crystal lattice and also the uniform charge distribution provided by mobile electrons. For these reasons they can be moulded into sheets and wires.
- d. They have high melting points and high densities due to the close packing of the positive ions in the crystal and due to high metallic bonding.

1.4.3 COVALENT OR NETWORK SOLIDS

In covalent solids, the constituent particles are non-metal atoms linked to the adjacent atoms by covalent bonds throughout the crystal. As a result, a network of covalent bond is formed. Hence, they form *giant molecules*.

Diamond and silicon carbide (SiC) (or called carborundum) are some examples of such solids. In diamond, the C-atoms are linked

together by covalent bond to give a three-dimensional structure.

Following are the characteristic properties of covalent solids:

- a. They are very hard and brittle since covalent bonds are strong and directional in nature.
- b. They have extremely high melting points and may even decompose before melting.
- c. They are insulators and do not conduct electricity.

Exception: Graphite is soft and a conductor of electricity. Its exceptional properties are due to its typical structure. The C-atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is a conductor of electricity due to these free electrons. Graphite is a soft solid and a good lubricant because different layers in graphite can slide over the other.

1.4.4 IONIC SOLIDS

In ionic solids, the constituent particles are positive and negative ions. Such solids are formed by the three-dimensional arrangement of positive (cations) and negative (anions) ions held by strong electrostatic (coulombic) force of attraction.

The characteristics of ionic solids are as follows:

- a. They have high melting and boiling points due to strong electrostatic force of attraction.
- b. They are electric insulators in the solid state because their ions are not free to move about. However, in the molten state or when dissolved in water, the ions become free to move about and hence they conduct electricity.
- c. They are soluble in polar solvents but insoluble in non-polar solvents.
- d. They are hard due to strong electrostatic forces of attractions and the ions are closely packed.
- e. They are brittle because their stability depends upon the retention of their geometrical pattern.

The different properties of the four types of crystalline solids are summarized in Table 1.2.

Table 1.2 Different types of solids

	Type of solid	Constituent particles	Bonding/ attractive forces	Examples	Physical nature	Electrical conductivity	Melting point
1.	Molecular solids a. Non-polar b. Polar c. Hydrogen bonded	Molecules	Dispersion or London forces dipole-dipole interactions Hydrogen bonding	Ar, CCl ₄ , H ₂ , I ₂ , CO ₂ HCl, SO ₂ H ₂ O (ice)	Soft Soft Hard	Insulator Insulator Insulator	Very low Low Low
2.	Metallic solids	Positive ions in a sea of delocalized electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high

3.	Covalent or network solids	Atoms	Covalent bonding	SiO ₂ (quartz), SiC, C (diamond), AlN, C _(graphite)	Hard Soft	Insulators Conductor (exception)	Very high
4.	Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF ₂	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High

1.5 TYPES OF SYMMETRY IN CRYSTALS

Crystals possess a regular, repetitive internal structure. The concept of symmetry describes the repetition of structural features. Crystals therefore possess symmetry, and crystallography is basically concerned with describing different types of symmetry. Broadly, two general types of symmetry exist. These consist of translational symmetry and point symmetry. Translational symmetry describes the periodic repetition of a structural feature across a length or through an area or volume. The concept of a lattice is directly related to the idea of a translational symmetry. Point symmetry, on the other hand, describes the periodic repetition of a structural feature around a point. Reflection, rotation, and inversion are all point symmetries. These are explained as below:

a. Reflection/plane of symmetry: It is an imaginary plane which passes through the centre of crystal and divides it into two equal portions such that one part is exactly the mirror image of the other. A cubic crystal such as NaCl possesses, in all, nine planes of symmetry: three rectangular and six diagonal planes of symmetry.

i. Rectangular plane of symmetry: These are the planes situated midway parallel to the opposite faces. Since a cube has six faces, so it has three rectangular planes of symmetry as shown in Fig. 1.4.

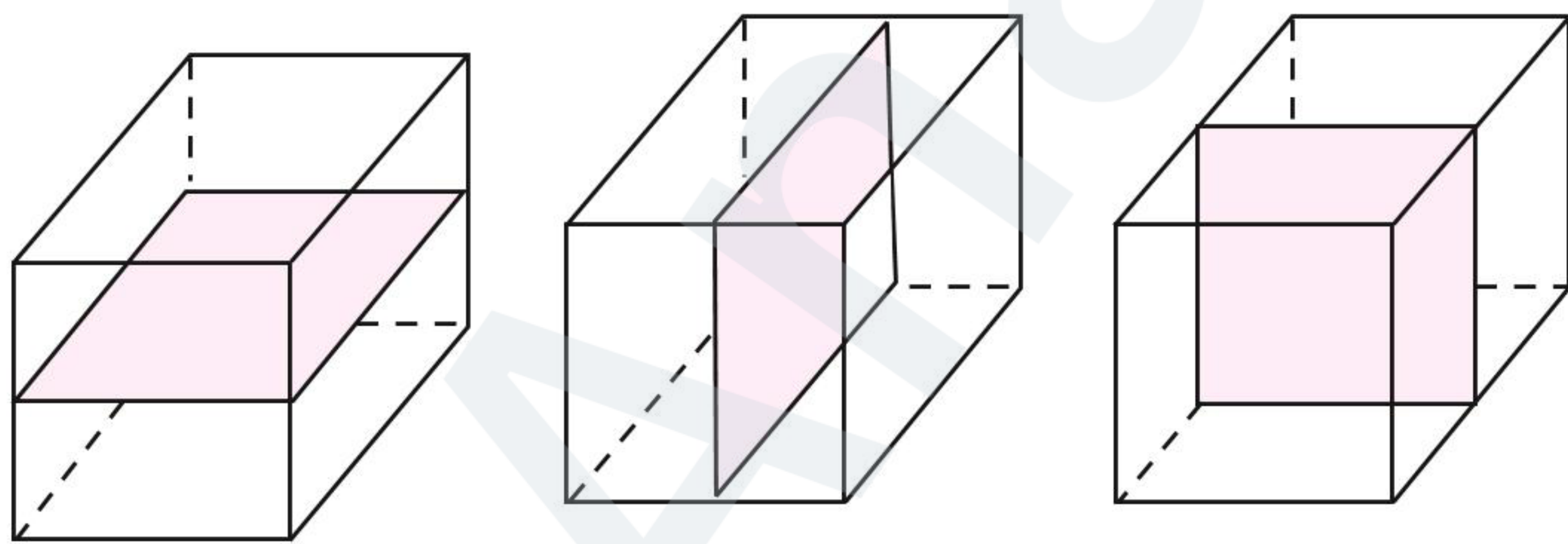


Fig. 1.4 Rectangular planes of symmetry

ii. Diagonal plane of symmetry: These are the planes touching the opposite edges. They lie on the diagonal of opposite faces. Since there are 12 edges or 6 pairs of opposite edges in a cubic crystal, as much as six diagonal planes of symmetry are possible in a cubic crystal (Fig. 1.5).

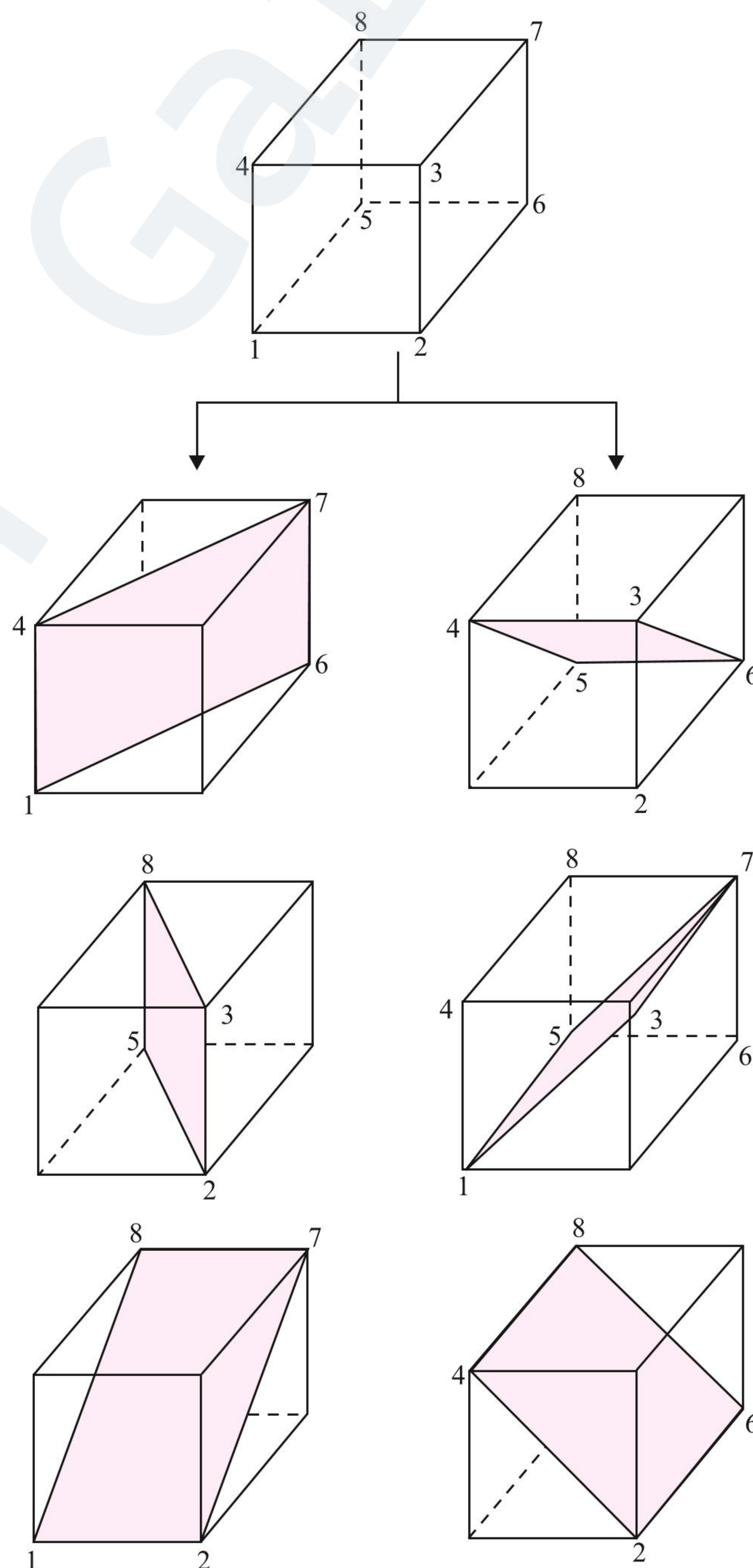


Fig. 1.5 Diagonal planes of symmetry

Thus, planes of symmetry in cubic crystal

= 3 rectangular planes of symmetry + 6 diagonal planes of symmetry

= 9 planes of symmetry

b. Rotational symmetry/axis of symmetry

Axis of line of symmetry: It is an imaginary line (or axis) about which the crystal may be related so that it presents the same appearance more than once in a complete rotation through 360° . In a cubic crystal, the axis of symmetry may be of three types depending upon the number of times the identical appearance occurs during the course of a complete rotation of 360° .

i. Axis of four-fold symmetry: Imagine a line passing through the centres of two opposite faces of a cube. On rotating the cube about this line as axis, the self coincidence (identical appearance) of the cube occurs four times during the course of rotation through 360° , i.e., the original appearance is repeated as a result of rotation through 90° . Such an axis is said to be an axis of four-fold symmetry or a tetrad axis. Now since there are six faces or three pairs of opposite faces in a cubic crystal, three such axes at right angle to each other are possible (Fig. 1.6).

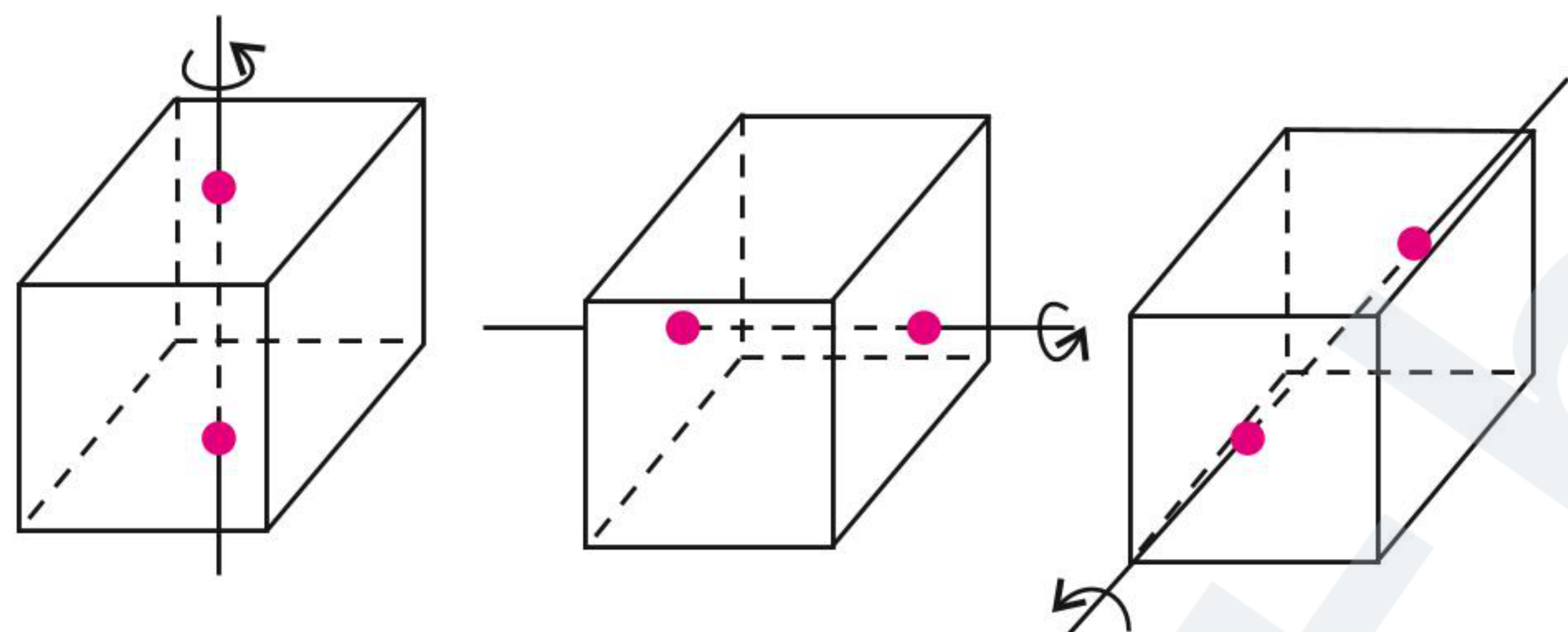


Fig. 1.6 Axis of four-fold symmetry

ii. Axis of two-fold symmetry: Imagine a line passing through the centres of the two diagonally opposite edges of a cube. On rotating the cube about this line as axis, the identical appearance of the cube occurs twice during the course of rotation through 360° , i.e., the original appearance is repeated as a result of rotation through 180° . Such an axis is said to be an axis of two-fold symmetry or a diad axis. Since there are 12 edges or six such diagonally opposite pairs of edges in a cubic crystal, six such axes are possible (Fig. 1.7).

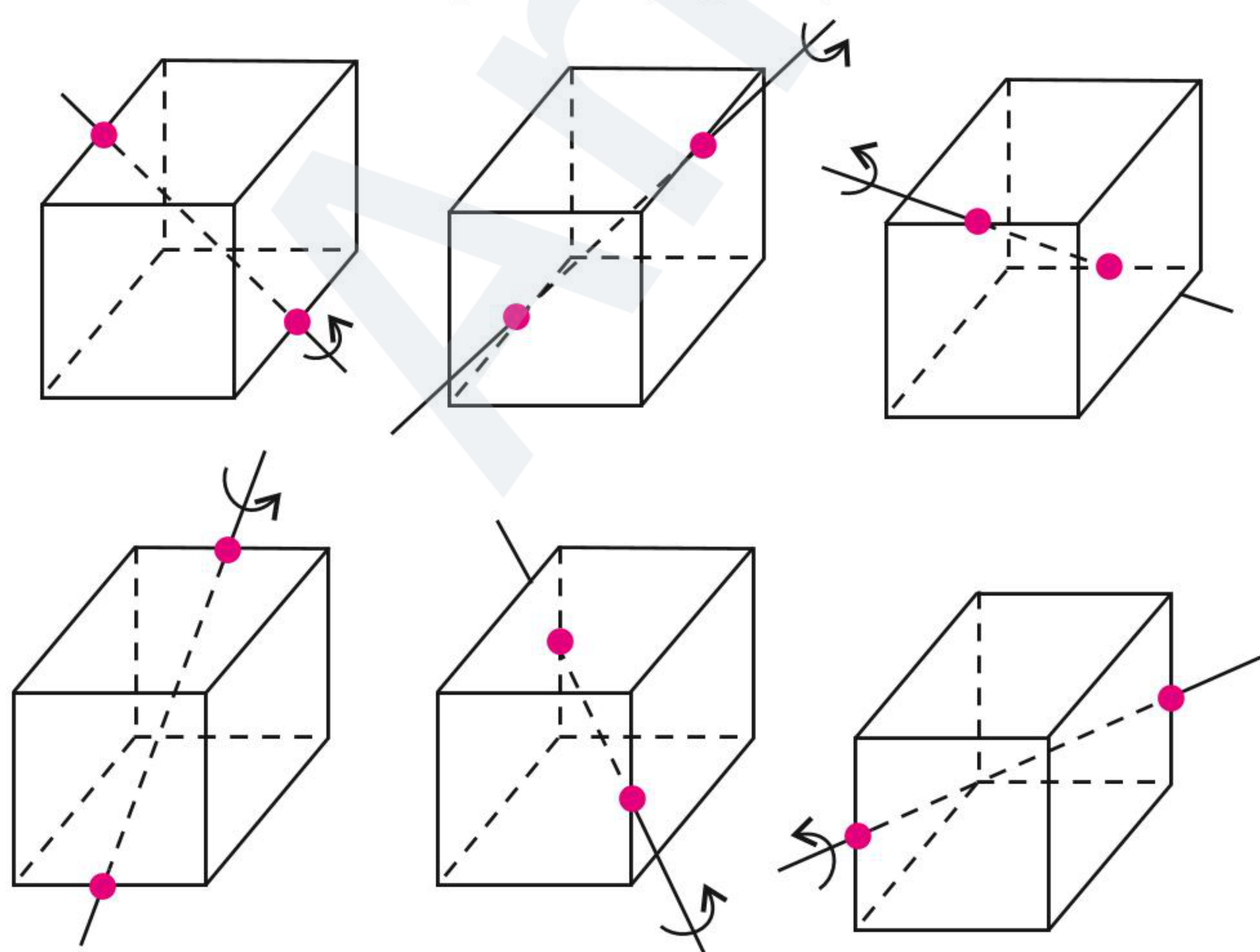


Fig. 1.7 Axis of two-fold symmetry

iii. Axis of three-fold symmetry: Imagine a line passing through the opposite corners of a cube along the body diagonal. On rotating the cube about this line as axis, the identical appearance of the cube occurs three times during the course of rotation through 360° , i.e., the original appearance is repeated as a result of rotation through 120° . Such axis is said to be an axis of three-fold symmetry or a triad axis. Now since there are eight corners or four such body diagonally opposite pairs of corners of cubic crystal, four such axes are possible (Fig. 1.8).

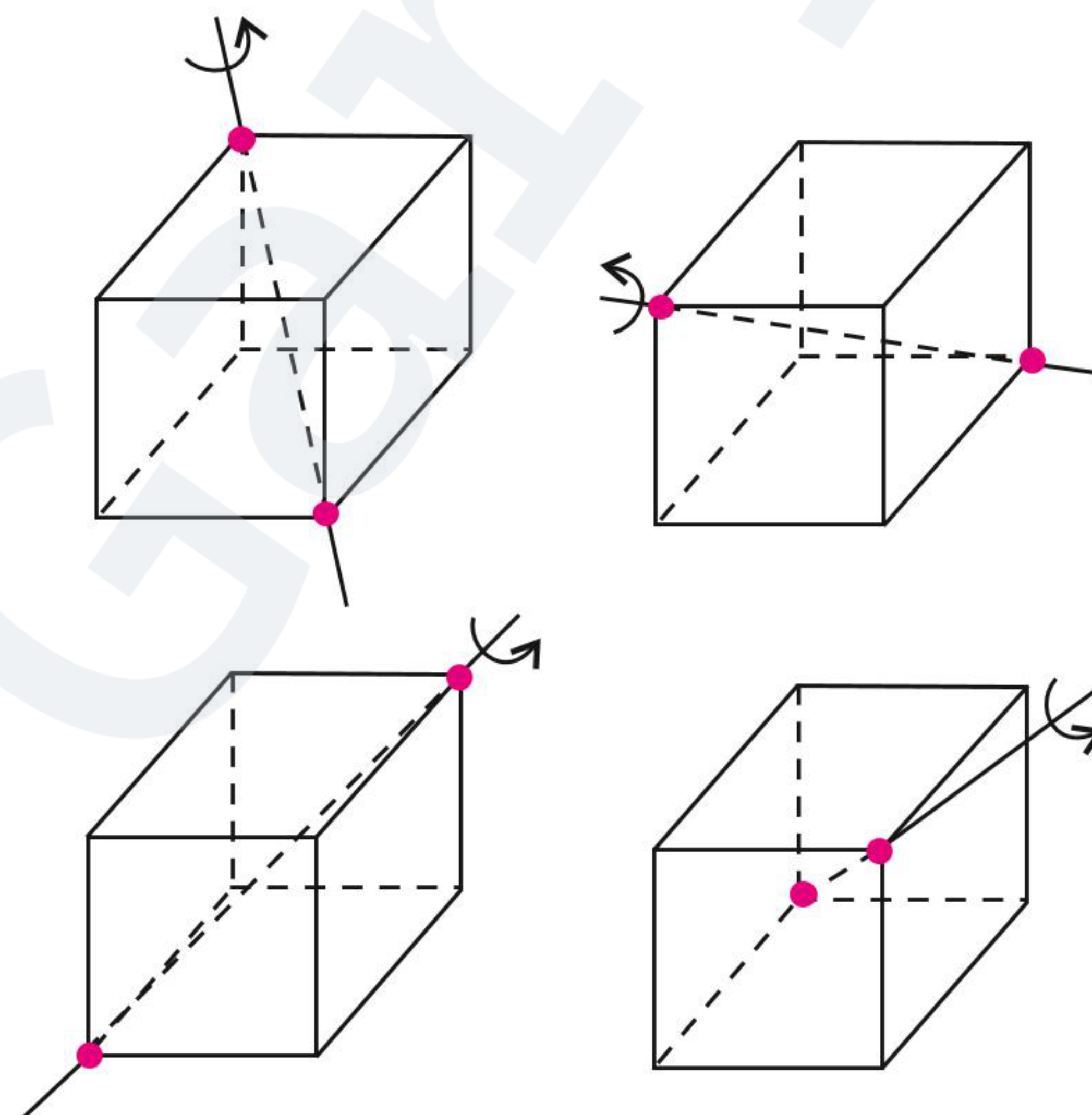


Fig. 1.8 Axis of three-fold symmetry

Thus, in a cubic crystal, there are three axes of four-fold symmetry, four axes of three-fold symmetry, and six axes of two fold symmetry. Thus, in all, a cubic crystal has $3 + 4 + 6 = 13$ axes of symmetry.

c. Inversion symmetry or centre of symmetry: It is such a point in the crystal that any line drawn through it intersects the surface of the crystal at equal distances on either side. A crystal may have one or more planes or axes of symmetry but it never has more than one centre of symmetry which lies at the centre of the cube (Fig. 1.9).

The total number of elements of symmetry in a cubic crystal are 23.

Planes of symmetry = $3 + 6 = 9$

Axes of symmetry = $3 + 4 + 6 = 13$

Centre of symmetry = 1

$\therefore$ Total number of elements of symmetry = $9 + 13 + 1 = 23$

Axis of six-fold symmetry: This axis of symmetry is possible in hexagonal crystals and not in cubic crystals. Imagine a line passing through the centres of two opposite hexagonal faces of a hexagonal crystal. On rotating the crystal (hexagonal) about this line as axis, the identical appearance of the hexagon occurs six times in the course of one complete rotation of 360° , i.e., the original appearance is repeated as a result of rotation through 60° . Such an axis is, therefore, known as axis of six-fold symmetry or a hexad axis.

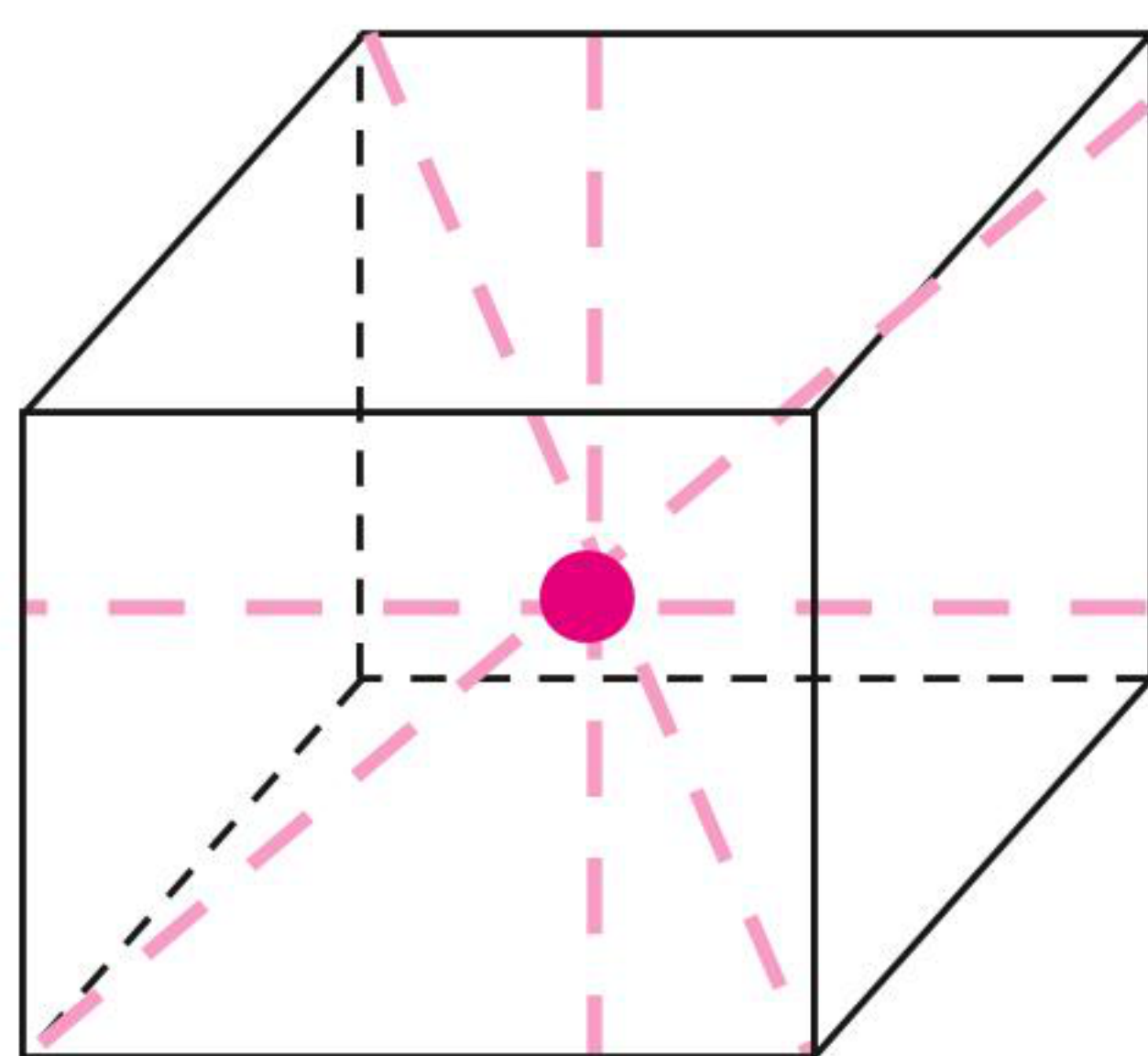


Fig. 1.9 Inversion symmetry/centre of symmetry

1.6 X-RAY STUDY OF CRYSTALS

a. X-ray diffraction: X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and synthetic materials.

It was suggested by Max von Laue, in 1913, that it might be possible to diffract X-rays by means of crystals. The reason for the suggestion was that the wavelength of X-rays was of about the same order (10^{-8} cm) as the inter-atomic distances in a crystal. In fact, Bragg succeeded in diffracting X-rays from sodium chloride crystals. This observation has proved to be highly useful in determining structures and dimensions of crystals as well as in the study of a number of properties of X-rays themselves.

b. Structure determination by X-ray: If we look through a piece of thin stretched cloth against bright light, we find a pattern caused by the deflection of light as it passes through the regular space threads of the fabric. The deflection of light is called diffraction and the patterns produced are called diffraction patterns. From the diffraction pattern, it is possible to deduce the arrangement of strands in the fabric. The same idea is used to determine the arrangement of atoms/ions in a crystal. Max von Laue visualized that a crystal can act as a three-dimensional grating for the diffraction of X-rays. In 1912, he obtained a diffraction pattern produced by passing X-rays through a crystal of copper sulphate. W.L. Bragg and his father W.H. Bragg determined the cubic structure of sodium chloride using X-rays. These days, the structure of extremely complex substances such as proteins and nucleic acids is determined using the technique.

When a beam of X-rays falls on a crystal plane composed of regularly arranged atoms or ions, the X-rays are diffracted. Waves from the diffracted X-rays may interfere and destroy each other (Fig. 1.10). However, it is also possible that X-rays diffracted by the particles (atoms/ions) can also reinforce each other producing constructive interference.

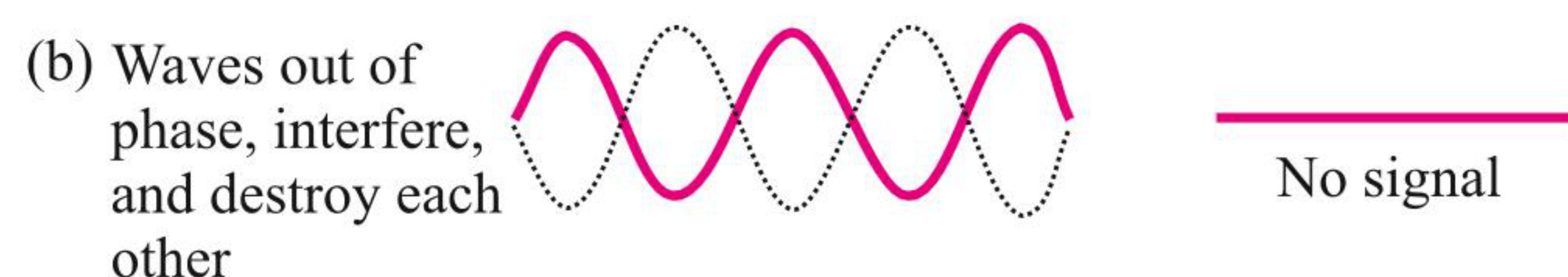
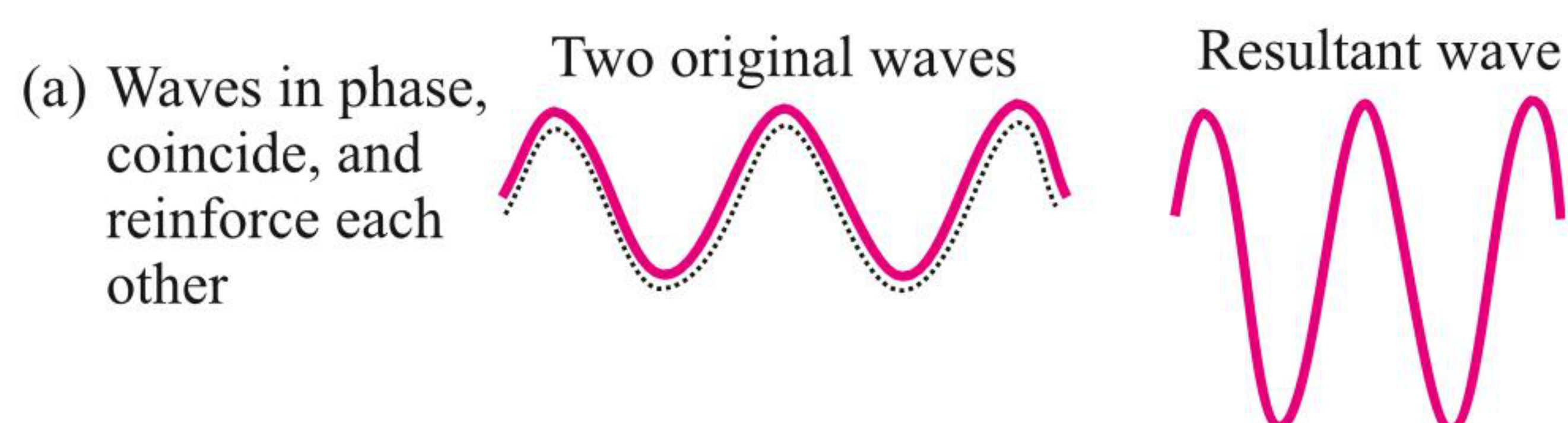


Fig. 1.10 (a) Constructive and (b) destructive interference of X-rays

In a crystalline solid, the constituent particles (atoms, ions, or molecules) are arranged in a regular order. An interaction of a particular crystalline solid with X-rays helps in investigating its actual structure.

Crystals are found to act as diffraction gratings for X-rays and this indicates that the constituent particles in the crystals are arranged in planes at close distances in repeating patterns.

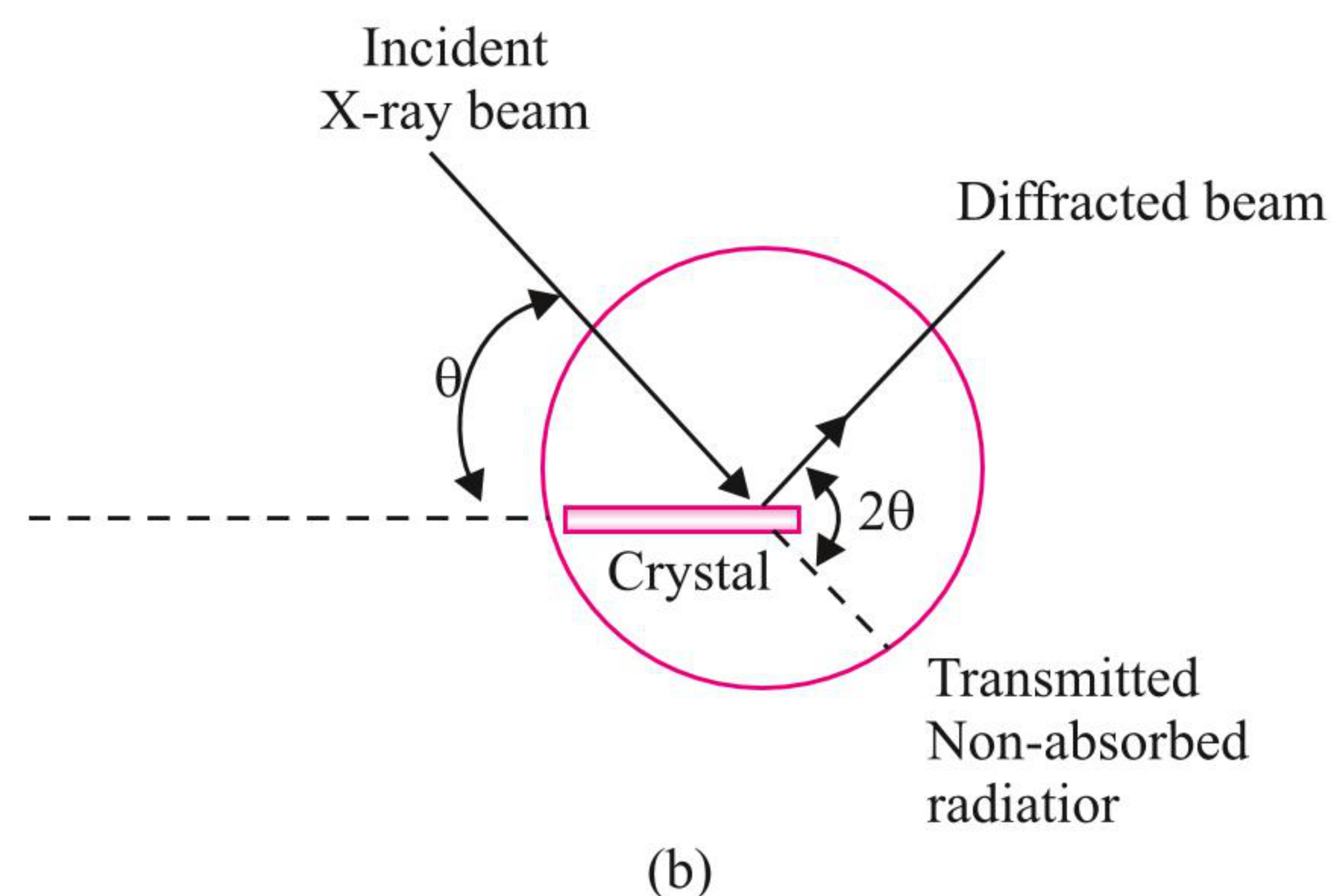
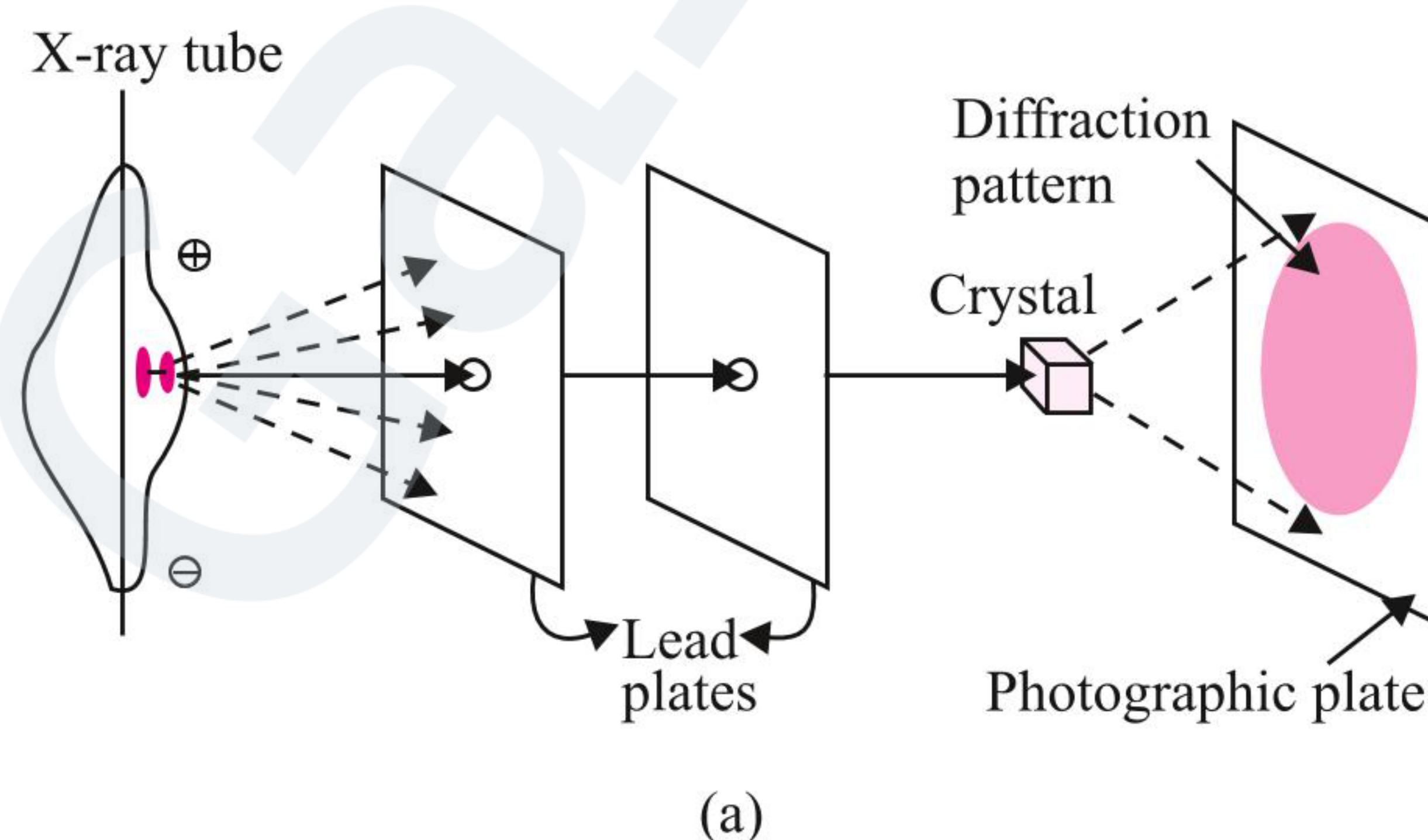


Fig. 1.11 Study of X-ray diffraction

A simple representation of the X-ray diffraction is shown in Figs. 1.11(a) and 1.11(b).

c. Bragg's equation

W.H. Bragg pointed out that the scattering of X-rays by crystals could be considered as reflection from successive planes of atoms in the crystals.

The process was based upon the principle that a crystal may be considered to be made up of a number of parallel equidistant atomic planes as represented by lines AB, CD, and EF in Fig. 1.12.

Assume two waves Y and Z of X-ray beams which are in phase fall on the surface of the crystal. If ray Y gets reflected from the first layer, i.e., AB line and ray Z is reflected from the second layer of atoms, i.e., CD line, then it is evident that as compared to ray Y, ray Z has to travel

a longer distance, equal to QRS in order to emerge out of the crystal. If waves Y and Z are in-phase (for the intensity of the reflected beam to be maximum) after reflection, the difference in distance travelled by the two rays must be equal to the integral multiple of wavelength, i.e., $n\lambda$ (for constructive interference).

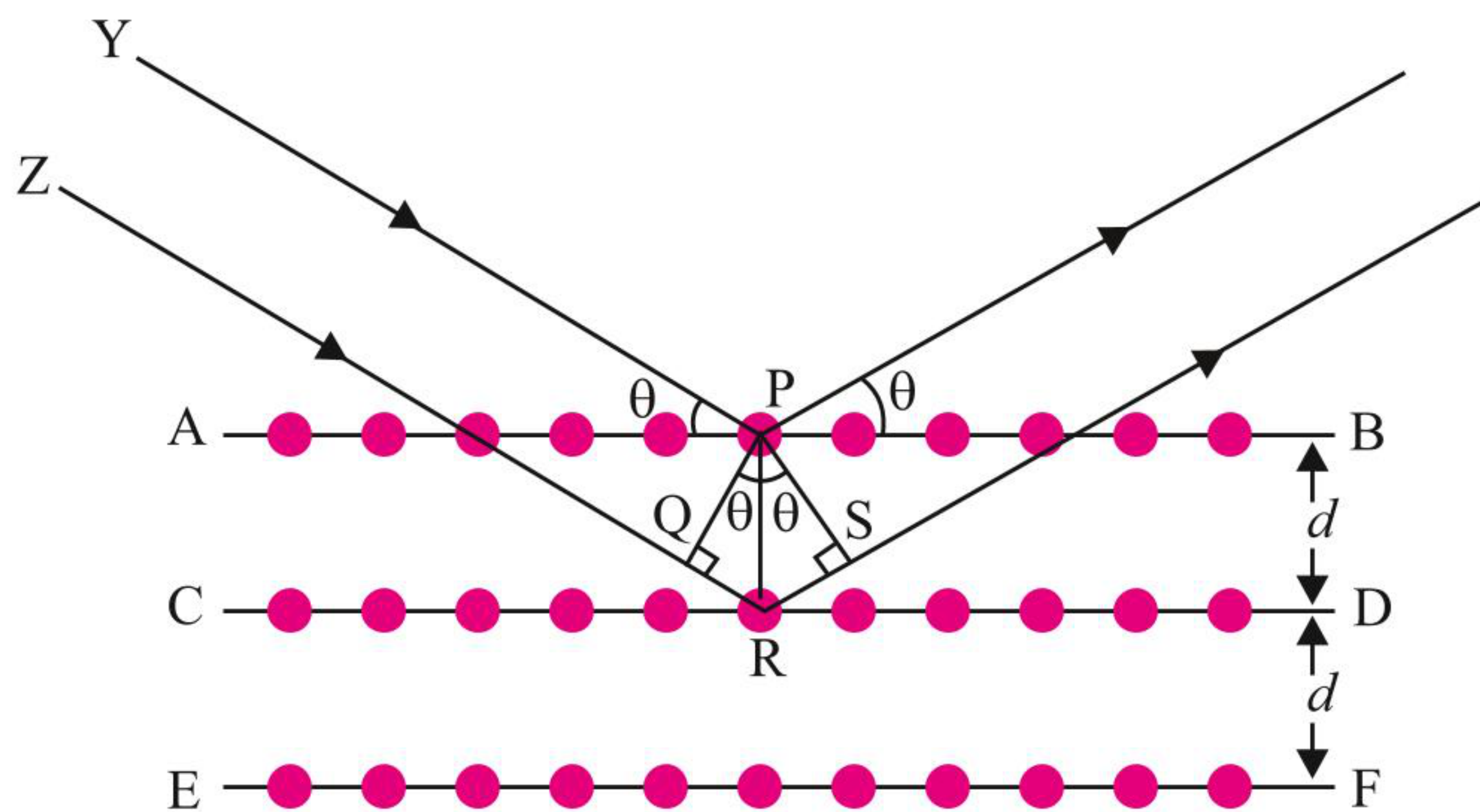


Fig. 1.12

Thus, distance $QRS = n\lambda$... (i)

It is obvious from the figure that $QR = RS = PR \sin \theta$

$\therefore QRS = 2PR \sin \theta$... (ii)

If the distance between the successive atomic planes is d , then, $PR = d$... (iii)

So, from Eqs. (i), (ii), and (iii), we have

$$n\lambda = 2d \sin \theta$$

This is Bragg's equation.

Thus, Bragg gave a mathematical equation to establish a relationship between the wavelength of the incident X-ray, the distance between the layers, and the angle of diffraction, where

λ = wavelength of X-ray used.

θ = angle between incident X-rays and the plane of the crystal. The diffracted beam makes an angle 2θ .

d = distance between planes of the constituent particles in a crystal.

n = an integer (1, 2, 3, 4, ...) which represents the serial order of diffracted beams.

For a given set of lattice planes, d has a fixed value. Therefore, the possibility of getting maximum reflection (i.e., the possibility of getting reflected waves in phase with one another) depends upon θ . If θ is increased gradually, a number of reinforced strong signals or positions will be found at which the reflections will be maximum. At these positions, n will have values equal to 1, 2, 3, Generally, in the experiments on X-ray reflections, n is set equal to 1. If λ is known, it is possible to determine d , the distances between atomic planes in the crystal by determining θ , experimentally. Similarly, if interplanar distances are given, the corresponding wavelengths of the incident beam of X-ray can be calculated.

ILLUSTRATION 1.1

A sample of a crystalline solid scatters a beam of X-rays of wavelength 70.93 pm at an angle 2θ of 14.66° . If this is a second-order reflection ($n = 2$), calculate the distance between the parallel planes of atoms from which the scattered beam appears to have been reflected.

Sol.

We know that: $n\lambda = 2d \sin \theta$

$$2\theta = 14.66^\circ \text{ or } \theta = 7.33^\circ$$

$$\lambda = 70.93 \text{ pm} = 70.93 \times 10^{-12} \text{ m}$$

$$\begin{aligned} \therefore d &= \frac{n\lambda}{2 \sin \theta} = \frac{2 \times 70.93 \times 10^{-12}}{2 \sin 7.33^\circ} \text{ m} \\ &= 556.3 \times 10^{-12} \text{ m} \\ &= 556.3 \text{ pm} \end{aligned}$$

ILLUSTRATION 1.2

Calculate λ of X-rays which give a diffraction angle $2\theta = 16.8^\circ$ for crystal, if the interplanar distance in the crystal is 0.2 nm and that only for the first-order diffraction is observed. Given $\sin 8.40^\circ = 0.146$.

Sol.

$$\begin{aligned} \lambda &= \frac{2d \sin \theta}{n} = \frac{2 \times 0.20 \times 0.146}{1} \quad (\text{since } \theta = 8.40^\circ) \\ &= 0.584 \text{ nm} \\ &= 5.84 \times 10^{-11} \text{ m} \end{aligned}$$

1.7 LATTICE

Before discussing the periodic patterns of atomic arrangements in crystals, let us examine the arrangements of points in space in periodically repeating patterns. This leads us to the concept of a space lattice. A space lattice provides the framework with reference to which a crystal structure can be described.

Definition: It is the periodic arrangement of the points such that the environment at any point is the same as that at any other point. Every point in lattice should have same surroundings.

As an example, consider a two-dimensional square array of points shown in Fig. 1.13. By repeated translation of the two vectors a and b on the plane of the paper, we can generate the square array. The magnitudes of a and b are equal and can be taken to be unity. The angle between them is 90° ; a and b are called the *fundamental translation vectors* that generate the square array. To ignore end effects near the boundary, we will assume that the array can be extended infinitely. If we locate ourselves at any point in the array and look out in a particular direction that lies on the plane of paper, the scenery will be same, irrespective of where we are.

Consider the immediate surroundings of a point in the array. If we look due north or due east from this point we see another point at a distance of 1 unit. Along northeast, we see the nearest point at a distance of $\sqrt{2}$ units and along north-northeast, the nearest

point is at a distance of $\sqrt{2}$ units. As this is true of every point in the array, it satisfies the definition given above and can be called a two-dimensional square lattice.

The main features of a lattice are as follows:

- A lattice should be infinite.
- Each point in a lattice is called lattice point.
- Lattice points are joined by straight lines to represent the geometry of lattice.
- A lattice is different from a crystal. In fact a lattice gives rise to crystal when points are replaced by particles such as atoms, ion, or molecules.

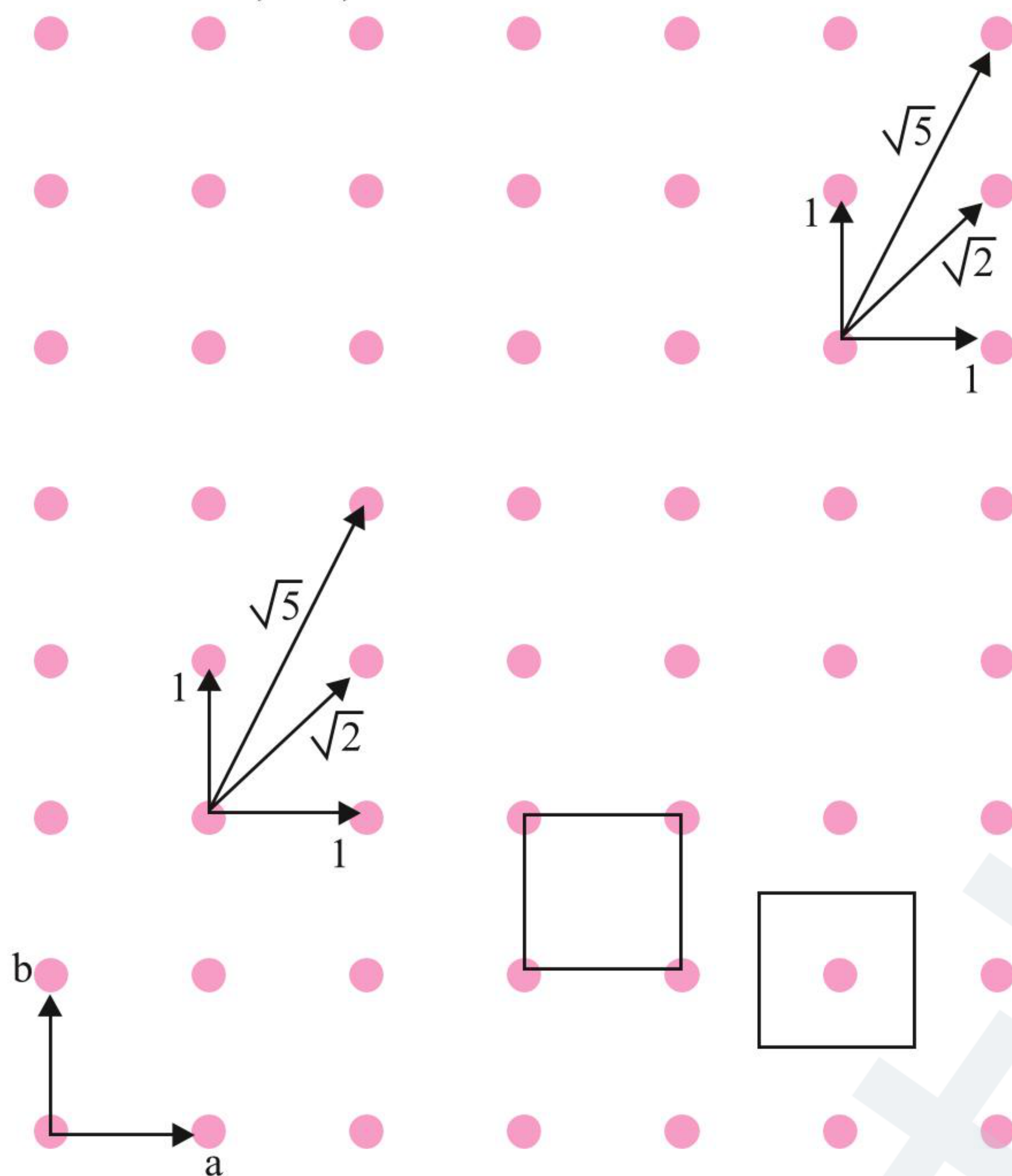


Fig. 1.13 Arrangement of points in space in periodically repeating pattern

1.7.1 FIVE TYPES OF TWO-DIMENSIONAL LATTICES

Space lattice is a regular repeating arrangement of points in space and forms the basis of the classification of all structures. For the sake of simplicity, let us understand the arrangement of points in two dimensions forming a two-dimensional lattice (Fig. 1.14).

There are five types of 2D-lattice (Fig. 1.14) which differ in the symmetry of the arrangement of points. They are: (a) hexagonal, (b) square, (c) rectangular, (d) rhombic, and (e) parallelogram.

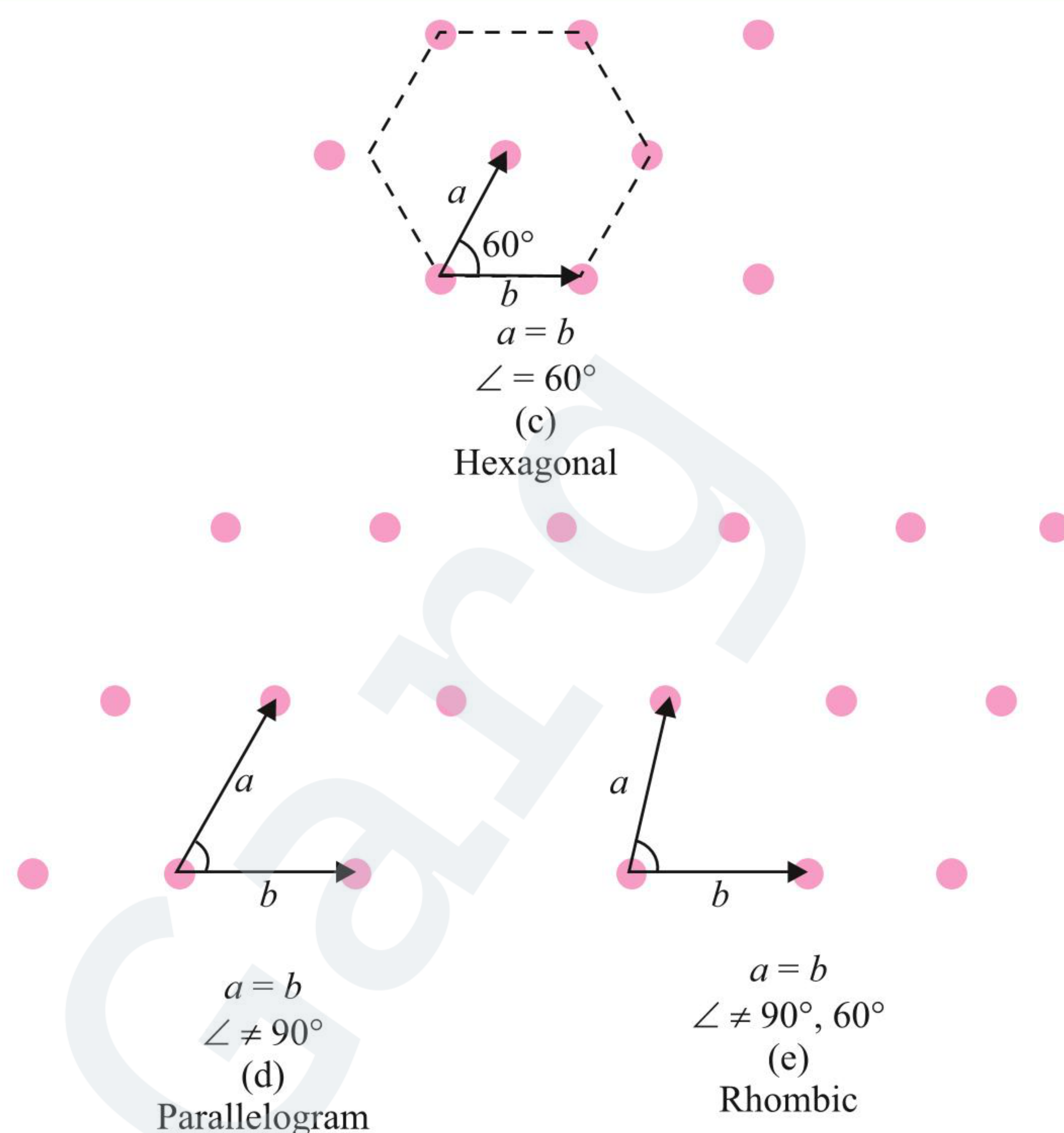
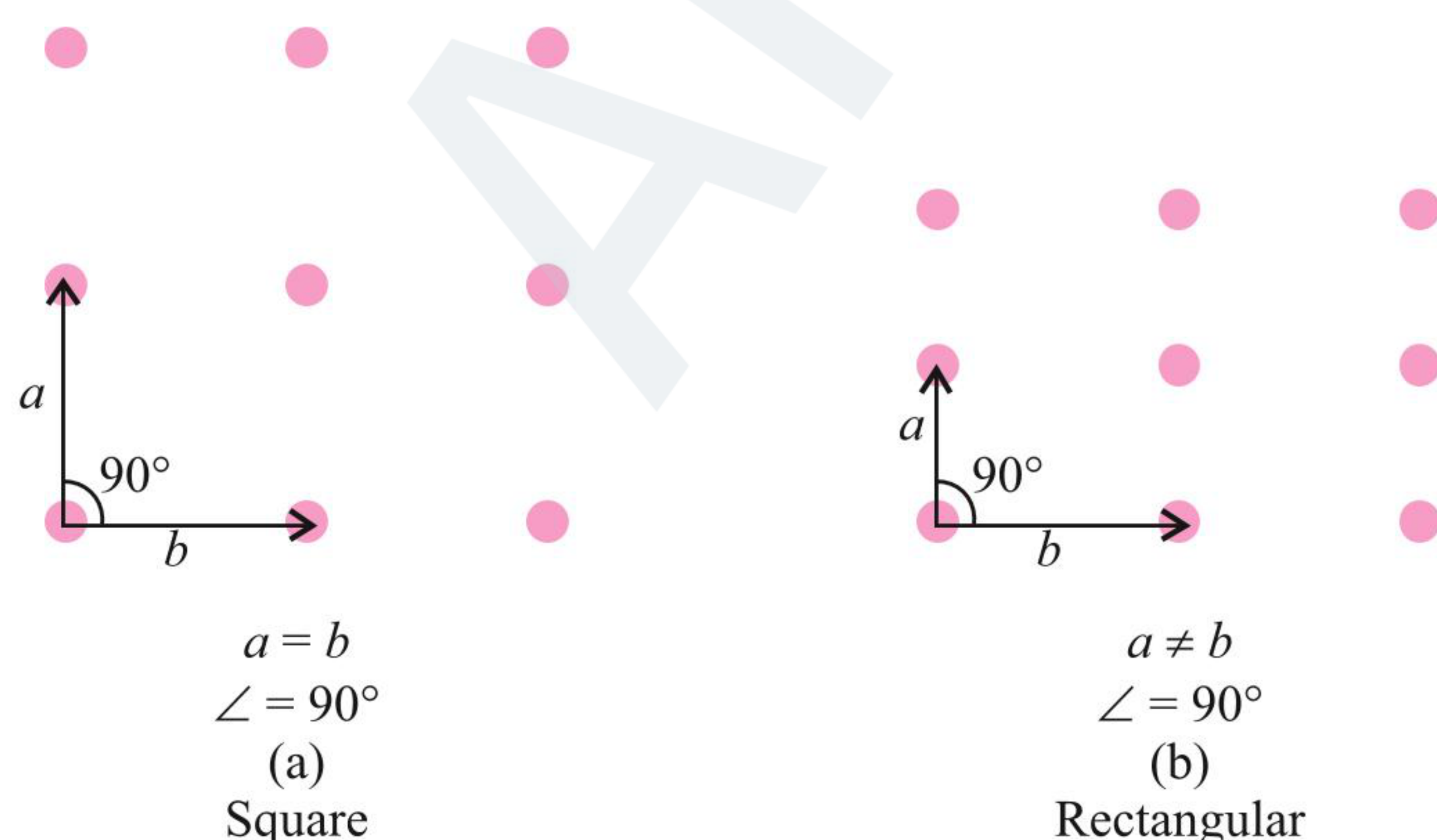


Fig. 1.14 Five types of 2-D lattice

Note: Pentagonal lattice is not possible because the interior angle of a regular pentagon is 108° which is not an integral factor of 360° .

A two-dimensional lattice is a regular arrangement of points. In order to specify it completely, only a small part of the lattice is described. Choose four points in a two-dimensional lattice and connect them to give a parallelogram. This figure is known as a *unit cell*.

A full lattice is generated by repeatedly moving the unit cell in the direction of its edges by a distance equal to the cell edge (Fig. 1.15).

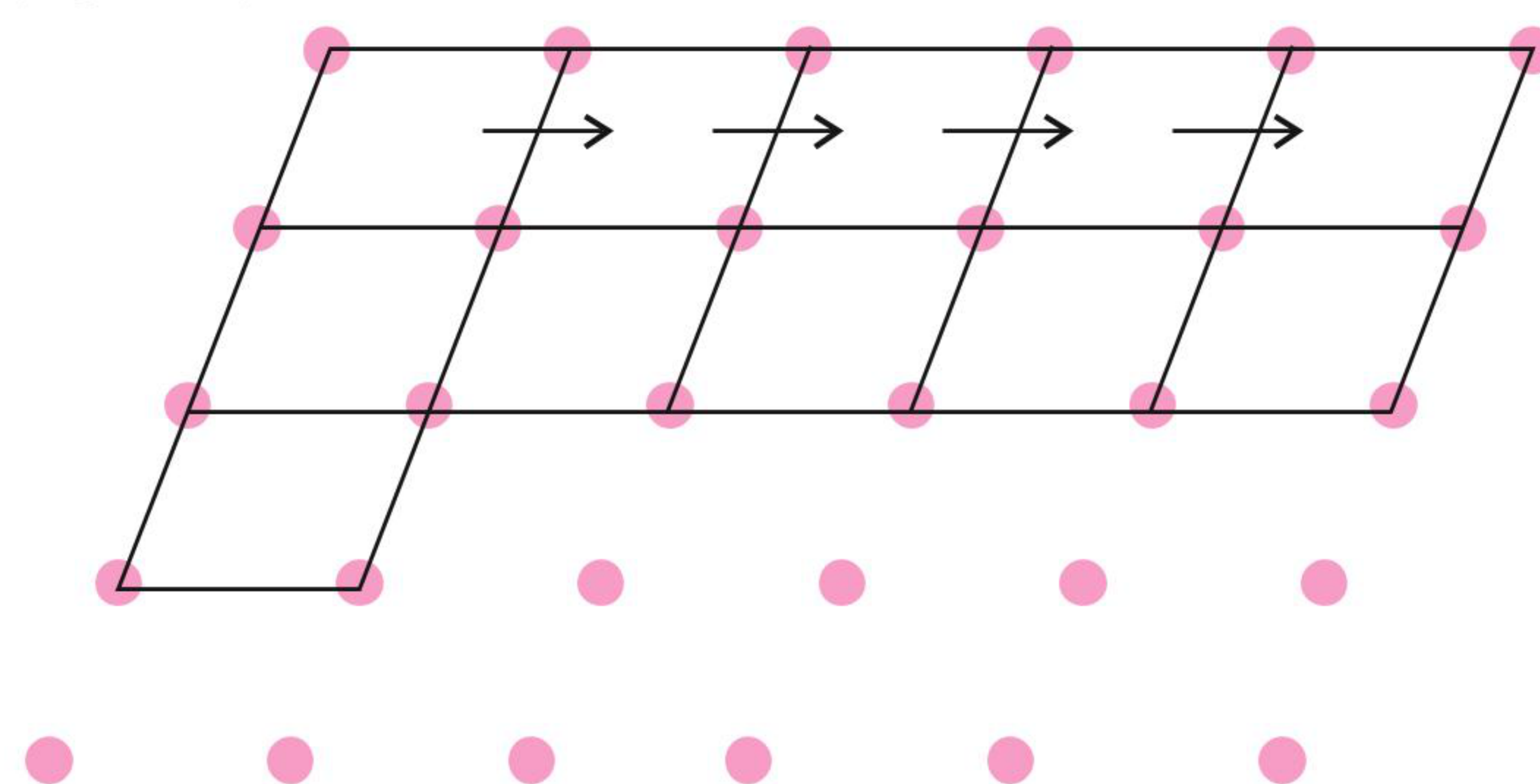


Fig. 1.15 Generation of an entire two-dimensional lattice by regular repetition of the unit cell in the direction of cell edges by distance equal to cell edge

For any lattice, a unit cell can be chosen in many different ways and may include any cell that has interior points. The smallest unit cell that shows the full symmetry of the lattice is most convenient.

The unit cells normally taken for square, rectangular, and parallelogram lattices are square, rectangle, and parallelogram, respectively. But for a hexagonal lattice, a rhombus with an angle of 60° is taken as the unit cell. However, a rectangular unit cell with an interior point is normally taken for the rhombic lattices.

A unit cell with an interior point is called a *centred unit cell*, in this case a centred rectangular unit cell. The unit cell that does not contain any interior point is known as *primitive unit cell*. Thus, for a two-dimensional lattice, a unit cell is specified by the length of its edges and the angle between them.

Note: For some lattices, the unit cell can be chosen in more than one way, as shown in Fig. 1.14(c). For the same lattice points, the unit cell may be a parallelogram, an equilateral triangle, or a regular hexagon with a lattice point in the centre.

In the first two unit cells, namely, parallelogram and equilateral triangle, all lattice points lie at the corners of the unit cell. Such unit cells are called “primitive unit cells.” The third one, i.e., hexagon, in which one lattice point also lies at the centre, is known as “non-primitive unit cell.”

The two-dimensional pattern is very common in the designs on many wallpapers and tiled floors. A complete two-dimensional pattern can be made by placing a motif (arrow) at a definite position at the lattice points (Fig. 1.16).

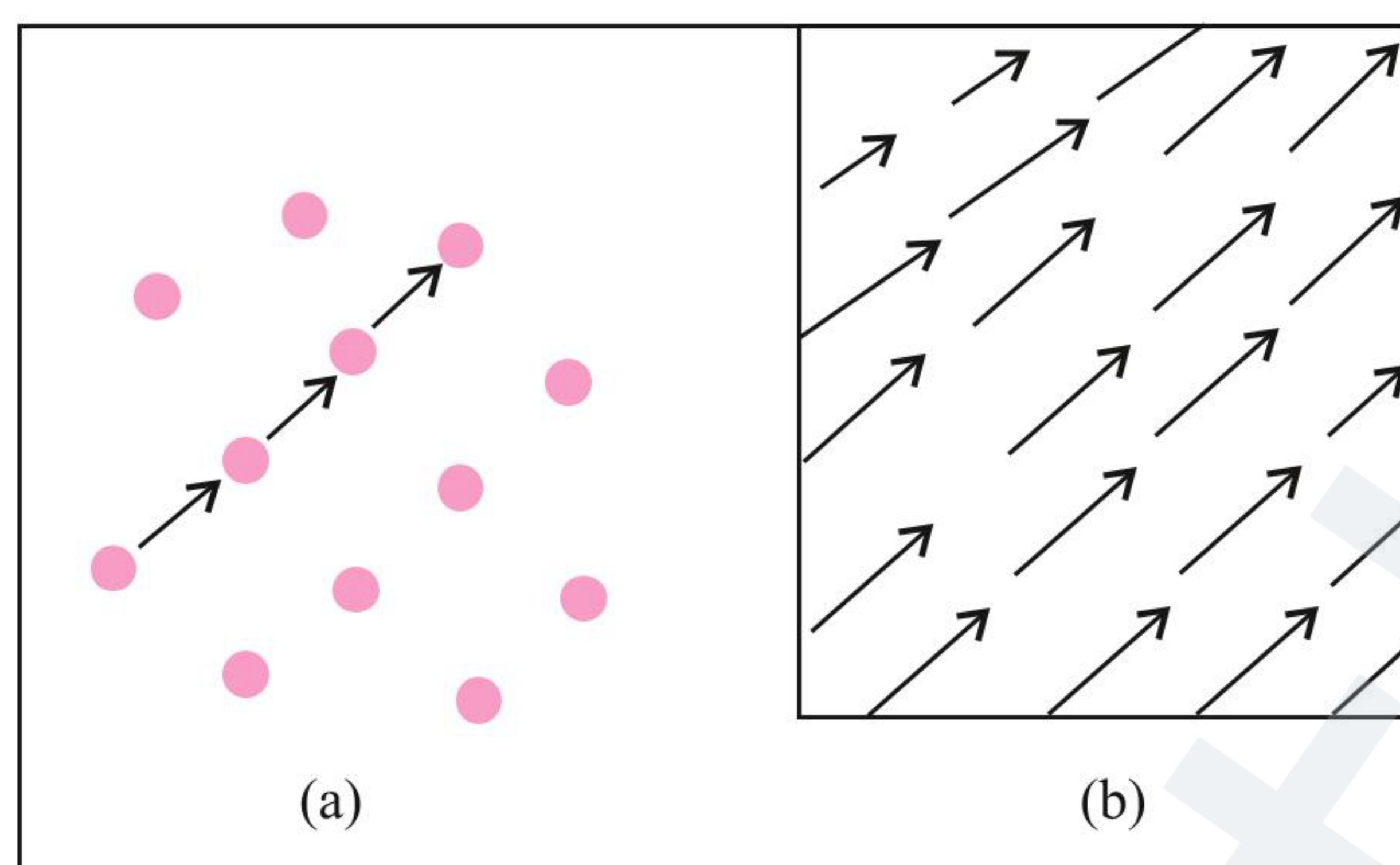


Fig. 1.16 Two-dimensional pattern

1.8 CRYSTAL LATTICES AND UNIT CELLS (3D)

The main characteristic of crystalline solids is a regular and repeating pattern of constituent particles. If the three-dimensional arrangement of constituent particles in the a crystal is represented diagrammatically, in which each particle is depicted as a point, the arrangement is called *crystal lattice*. Thus, a regular three-dimensional arrangement of points in space is called a crystal lattice. A portion of a crystal lattice is shown in Fig. 1.17.

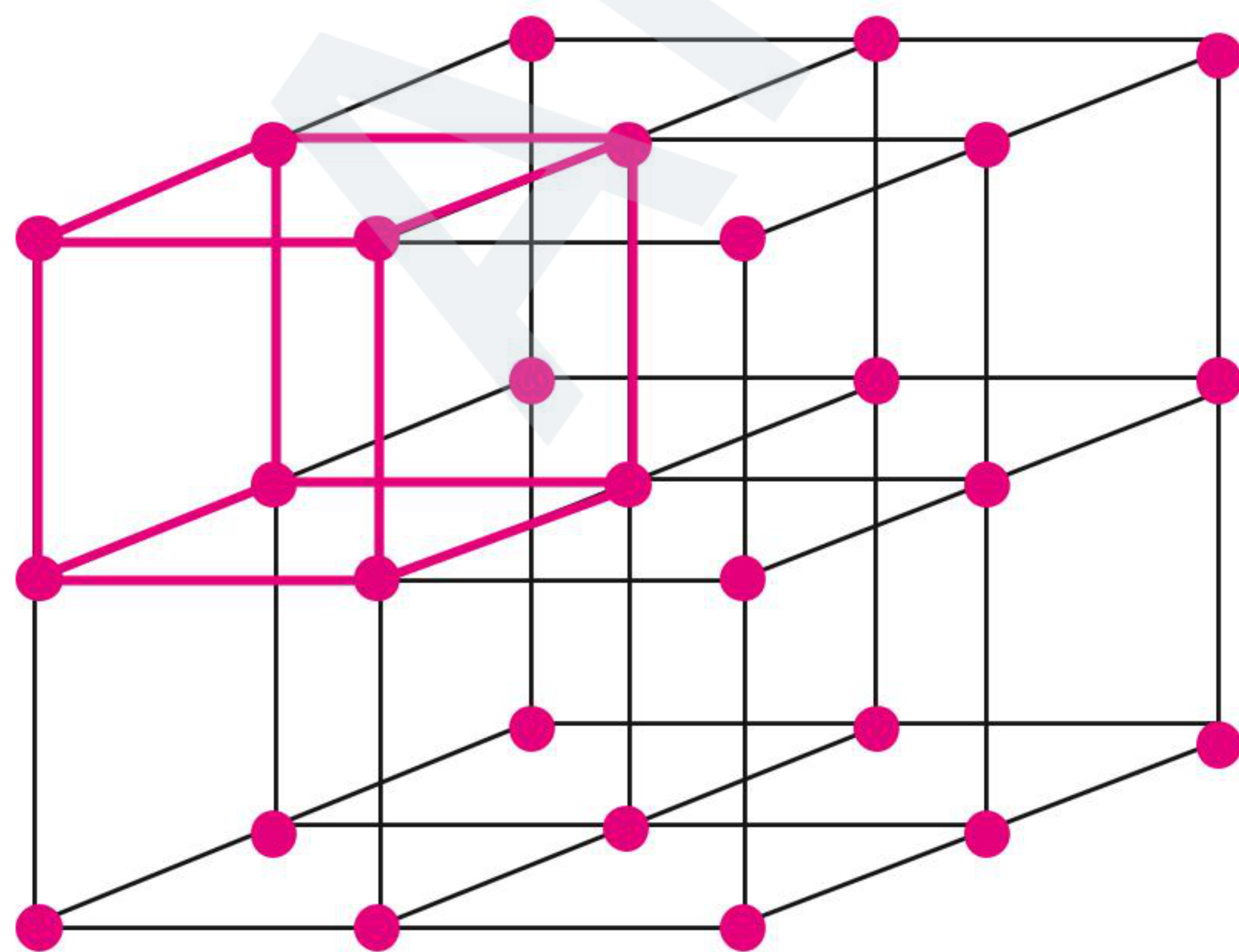


Fig. 1.17 A portion of a three-dimensional cubic lattice and its unit cell

Just as there are five possible two-dimensional lattices, there are 14 possible three-dimensional lattices. These are called *Bravais lattices* (after the French mathematician who first described them). The following are the characteristics of a crystal lattice:

- Each point in a lattice is called lattice point or lattice site.
- Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms), or an ion.
- Lattice points are joined by straight lines to bring out the geometry of the lattice.
- Unit cell is the smallest portion of a crystal lattice which, when repeated in different directions generates the entire lattice.

A unit cell is characterized by:

- Its dimensions along the three edges, a , b , and c . These edges may or may not be mutually perpendicular.
- angles between the edges: α (between b and c), β (between a and c), and γ (between a and b). Thus, a unit cell is characterized by six parameters, a , b , c , α , β , and γ . These parameters of a typical unit cell are shown in Fig. 1.18.

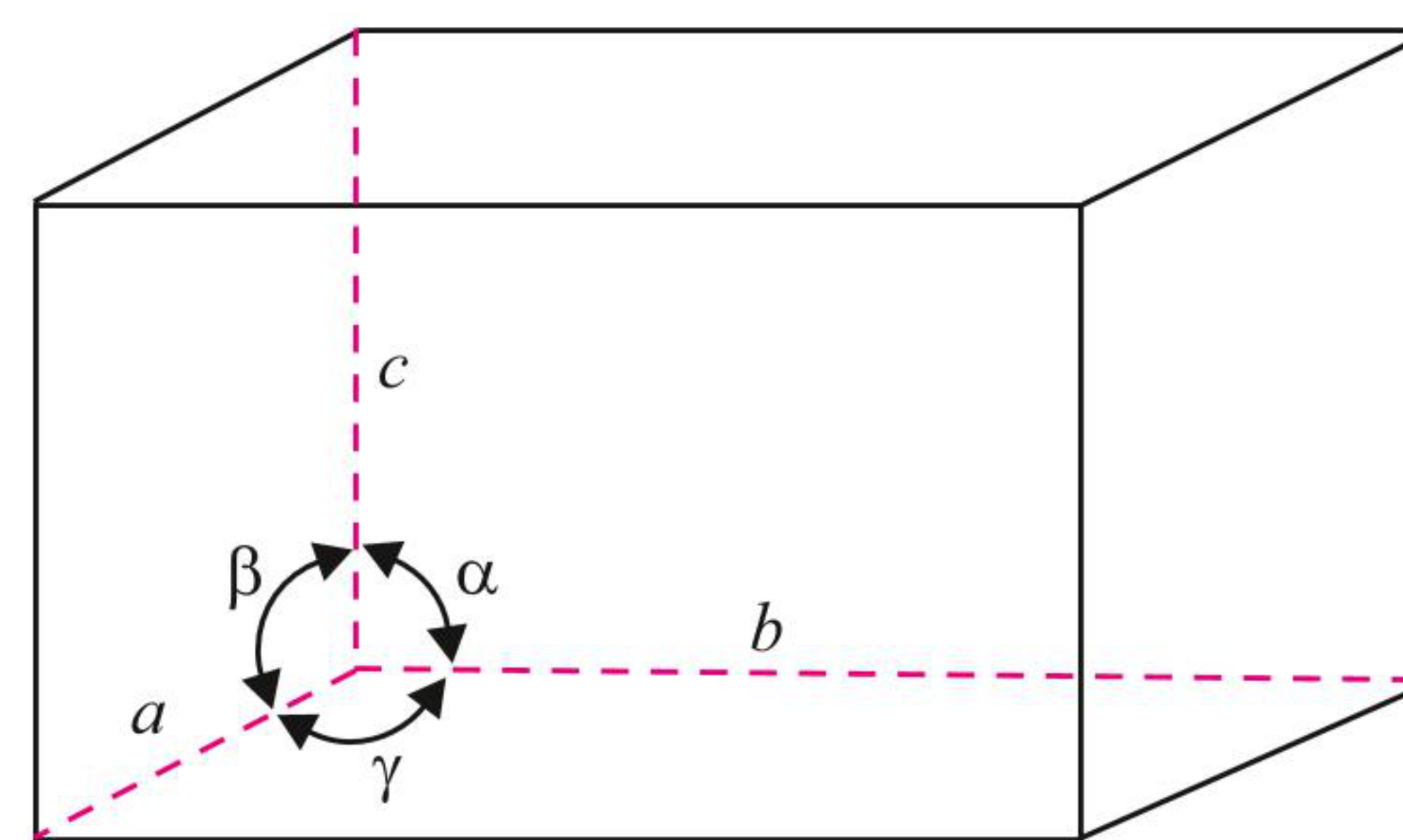


Fig. 1.18 Illustration of parameters of a unit cell

1.8.1 PRIMITIVE AND CENTRED UNIT CELLS

Unit cells can be broadly divided into two categories: primitive and centred unit cells.

Primitive Unit Cells

When constituent particles are present only on the corner positions of a unit cell, it is called as primitive unit cell.

Centred Unit Cells

When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centred unit cell. Centred unit cells are of three types:

- Body-centred units cells:** Such a unit cell contains one constituent particle (atoms, molecule, or ion) at its body centre besides the ones that are at its corners [Fig. 1.19(b)].
- Face-centred unit cells:** Such a unit cell contains one constituent particle present at the centre of each face, besides the ones that are at its corners [Fig. 1.19(c)].
- End-centred unit cell:** In such unit cells, one constituent particle is present at the centre of any two opposite faces or alternative faces, besides the ones present at its corners [Fig. 1.19(d)].

In all, there are seven types of primitive unit cells and these seven crystal systems have 14 types of Bravais lattices (Tables 1.3 and 1.4)

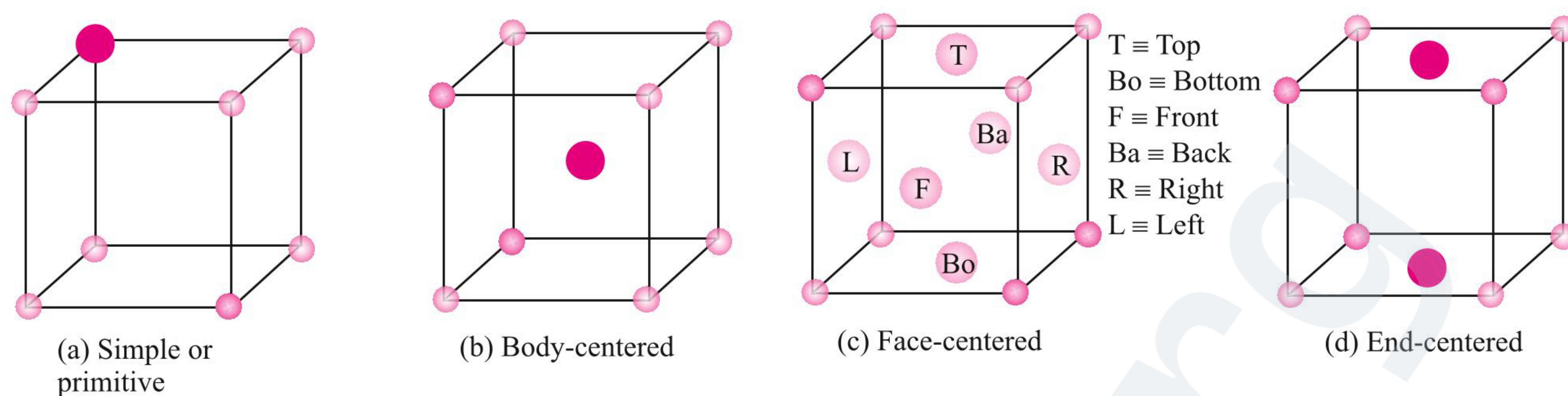


Fig. 1.19 Types of primitive/centred unit cells on the basis of the presence of their constituent particles

1.8.2 SEVEN CRYSTAL SYSTEM

The crystallographers have been able to divide 32 point groups and 14 space lattices into seven crystal systems and 14 space or Bravais lattices. Their characteristics along with the central unit cells they can form have been listed in Table 1.3 and in Figs. 1.20 and 1.21.

Table 1.3 Seven primitive unit cells and their possible variations as central unit cell

S.No.	Crystal system	Space or Bravais lattices	Total Bravais elements length	Minimum symmetry or edge	Axial distance	Axial angles	Examples
1.	Cubic	Primitive Body-centred Face-centred	3	4 three-fold 3 four-fold	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, KCl ZnS, diamond, Cu
2.	Ortho-rhombic	Primitive Body-centred Face-centred End-centred 2-axis	4	Three mutually perpendicular 2-fold (or)	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 BaSO_4 , K_2SO_4
3.	Tetragonal	Primitive Body-centred	2	1 four-fold axis of symmetry	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White Sn, SnO_2 , TiO_2 , CaSO_4 , NH_4Br
4.	Monoclinic	Primitive end-centred	2	1 two-fold axis of symmetry	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$	Monoclinic sulphur, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
5.	Triclinic	Primitive	1	1 one-fold axis of symmetry	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ $\text{K}_2\text{Cr}_2\text{O}_7$, H_3BO_3
6.	Hexagonal	Primitive	1	1 six-fold axis of symmetry	$a = b \neq c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	Graphite, ZnO, CdS
7.	Rhomo-bohedral or Trigonal	Primitive	1	1 three-fold axis of symmetry	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite (CaCO_3), HgS (cinnabar), NaNO_3 , ICl
			Total = 14				

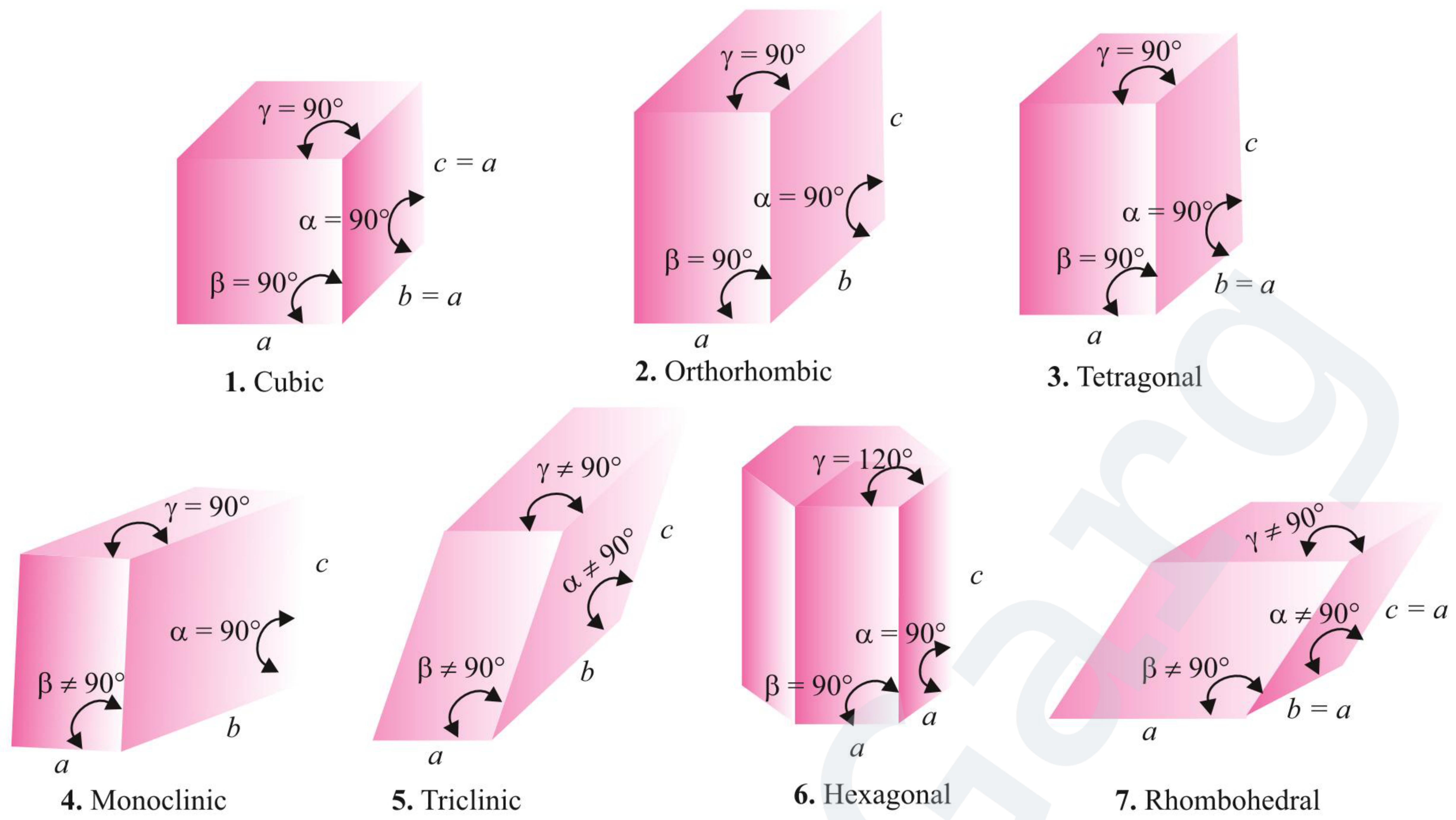
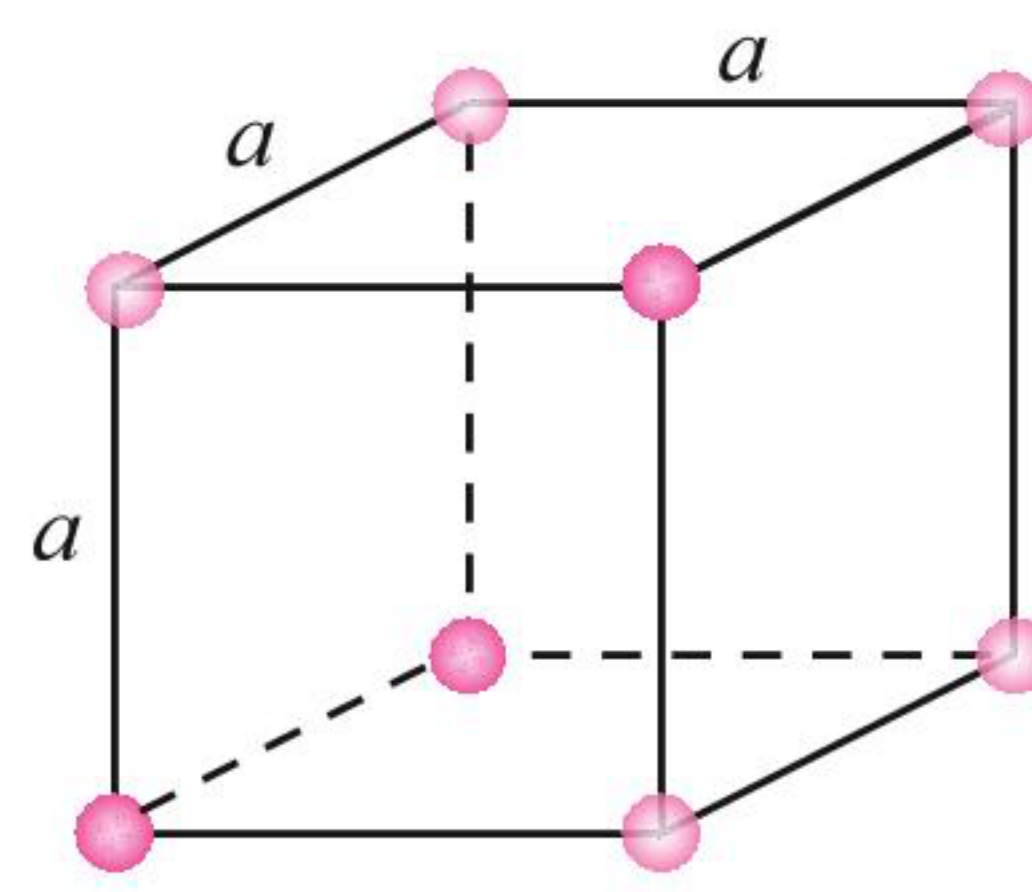
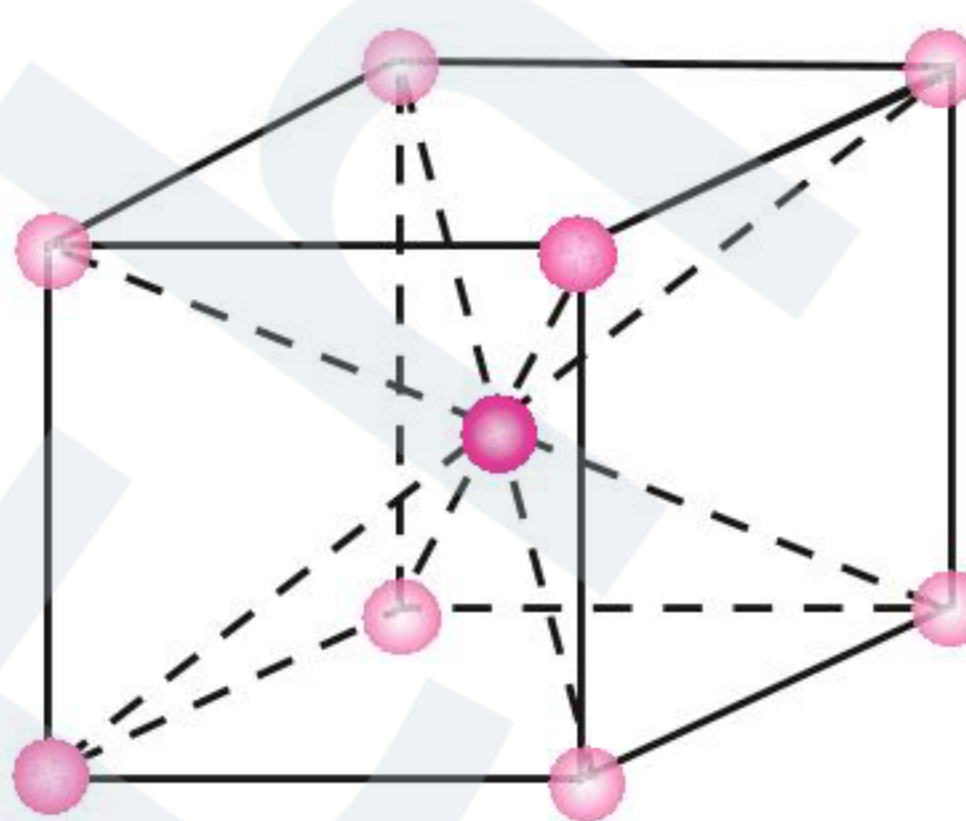


Fig. 1.20 Seven primitive unit cell in crystals

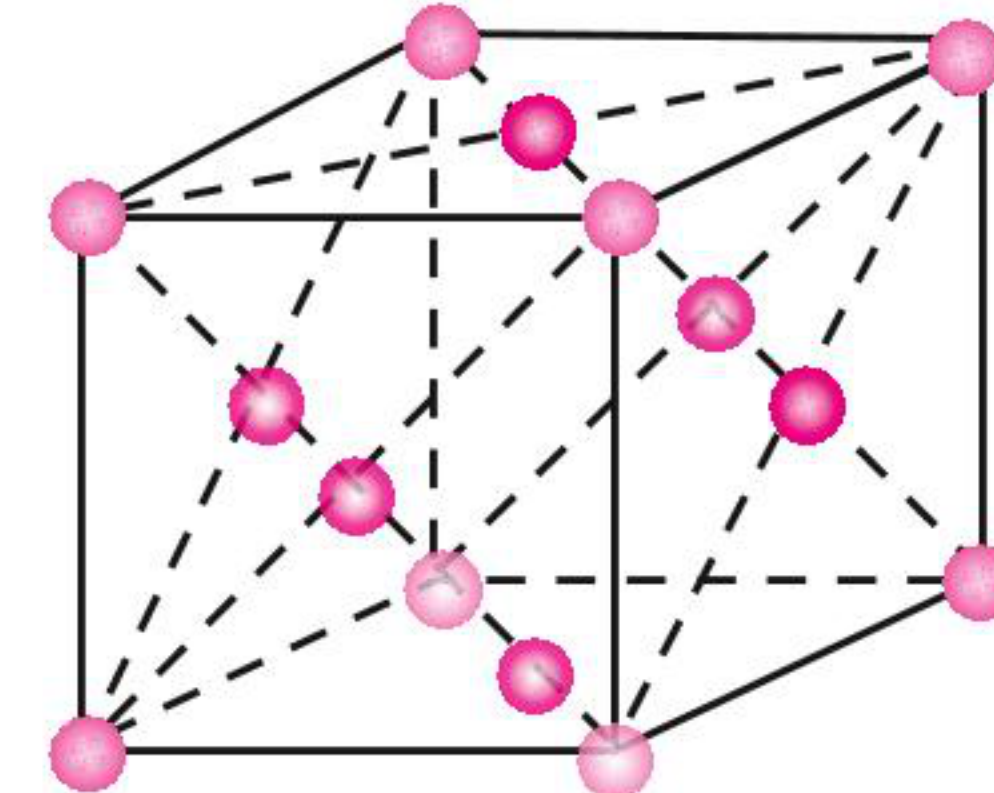
1. Cubic: All sides of same length between faces are all 90°



i. Primitive (or simple)

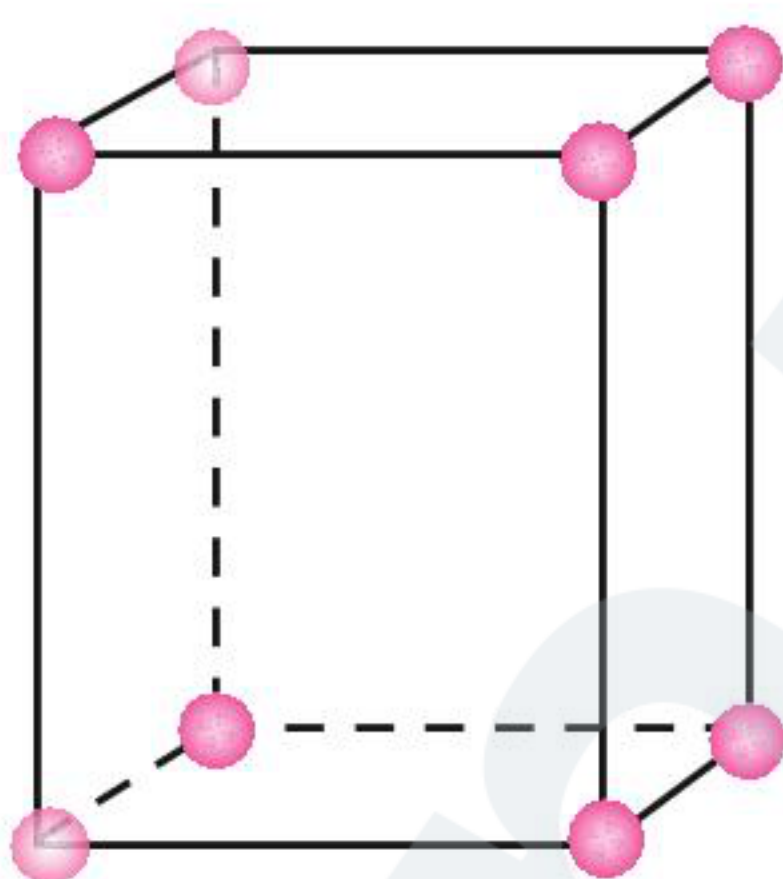


ii. Body-centered

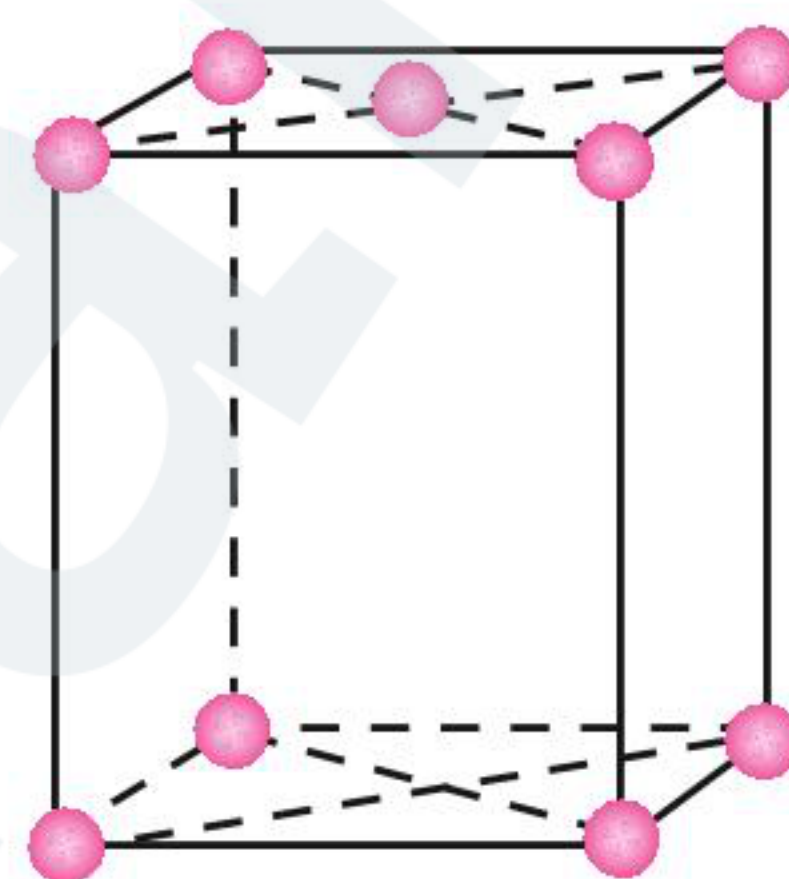


iii. Face-centered

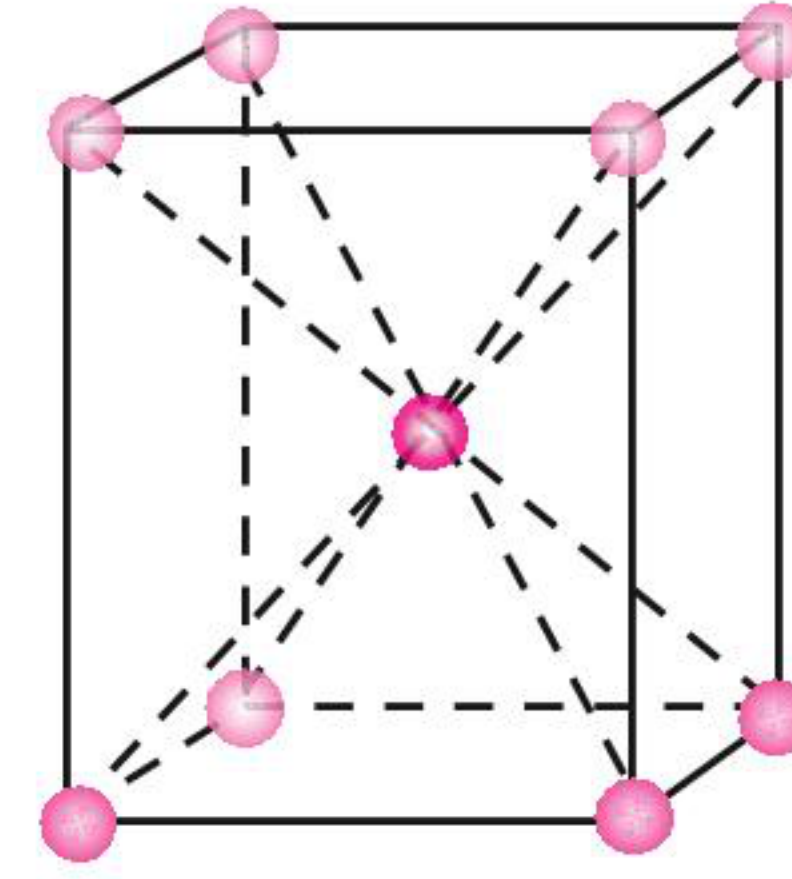
2. Orthorhombic: unequal sides, angles between faces all 90°



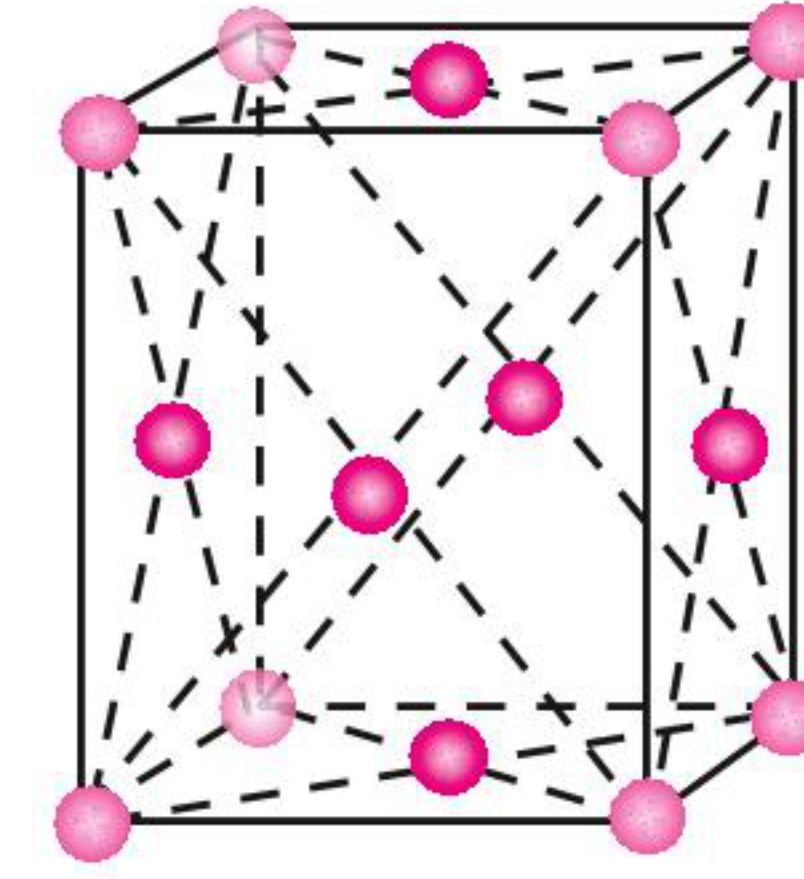
i. Primitive



ii. End-centered

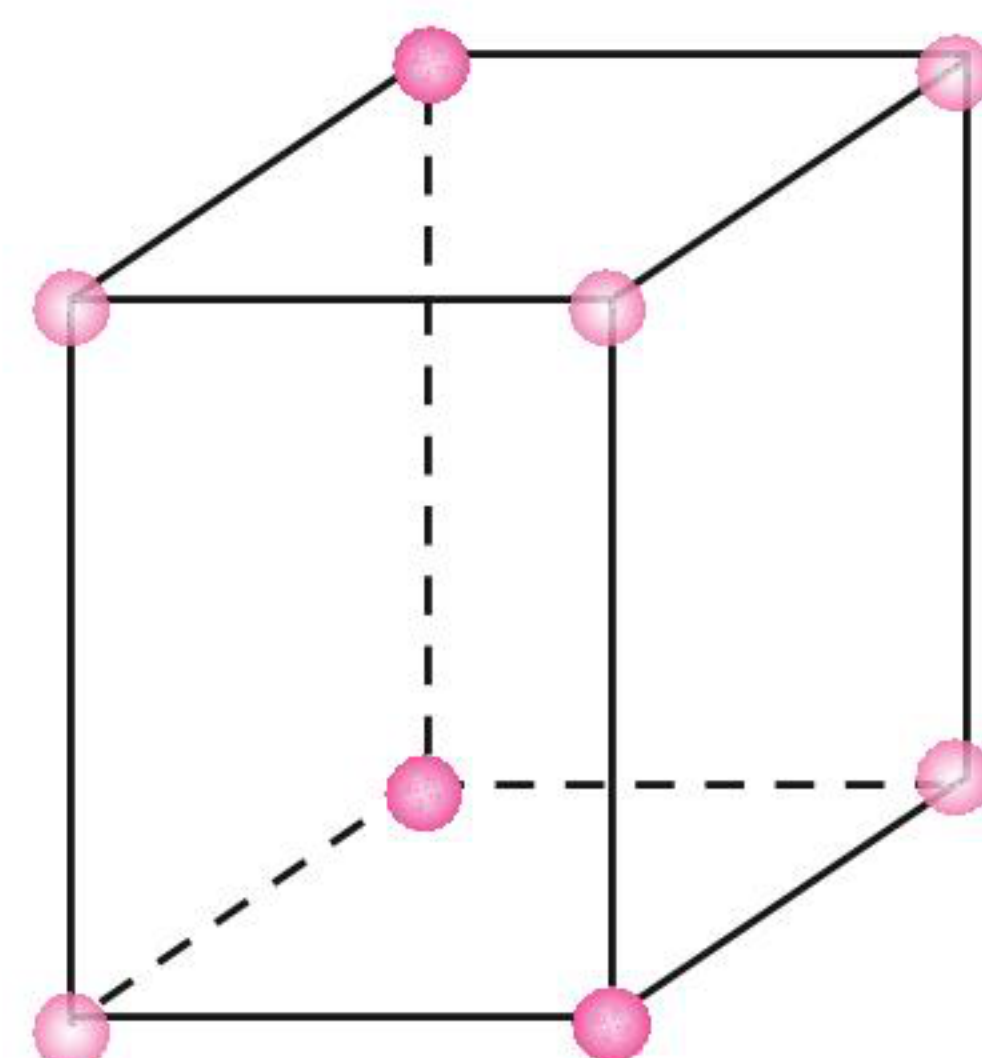


iii. Body-centered

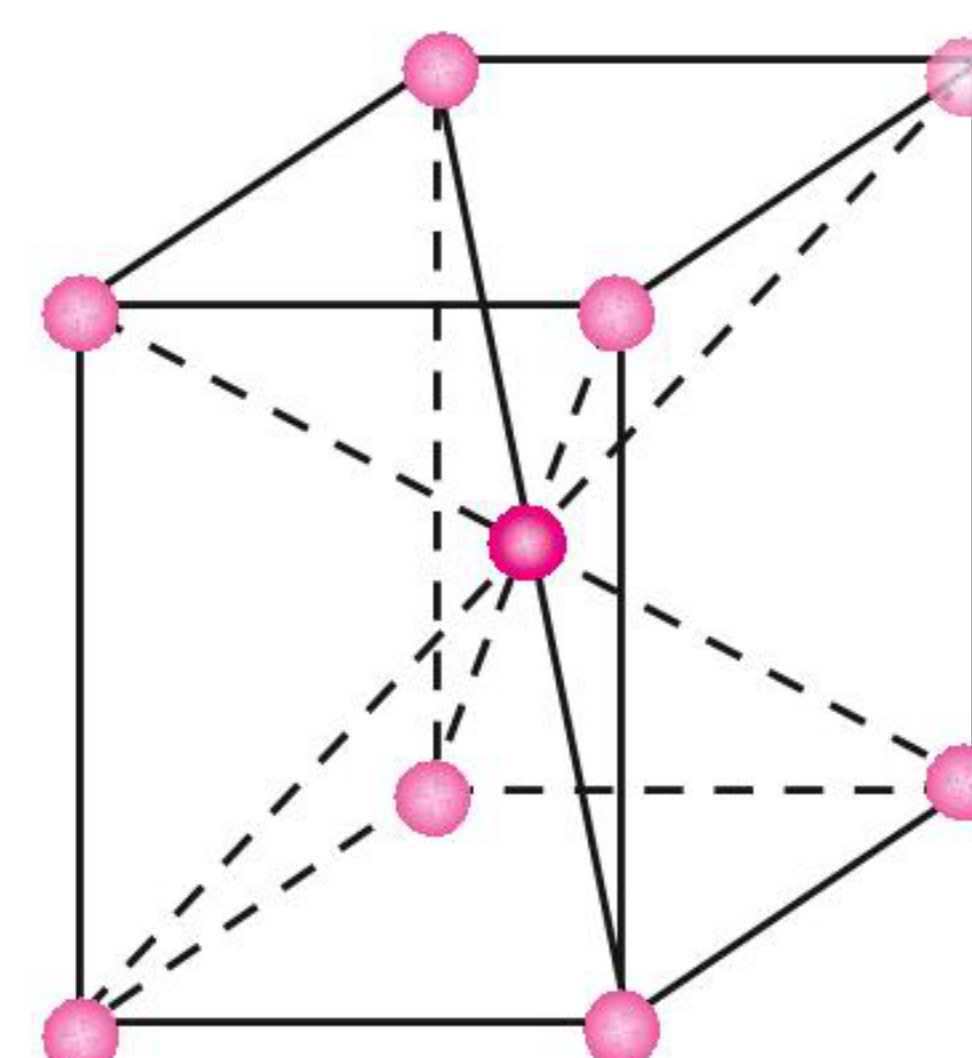


iv. Face-centered

3. Tetragonal: one side different in length to the other, two angles between faces all 90°

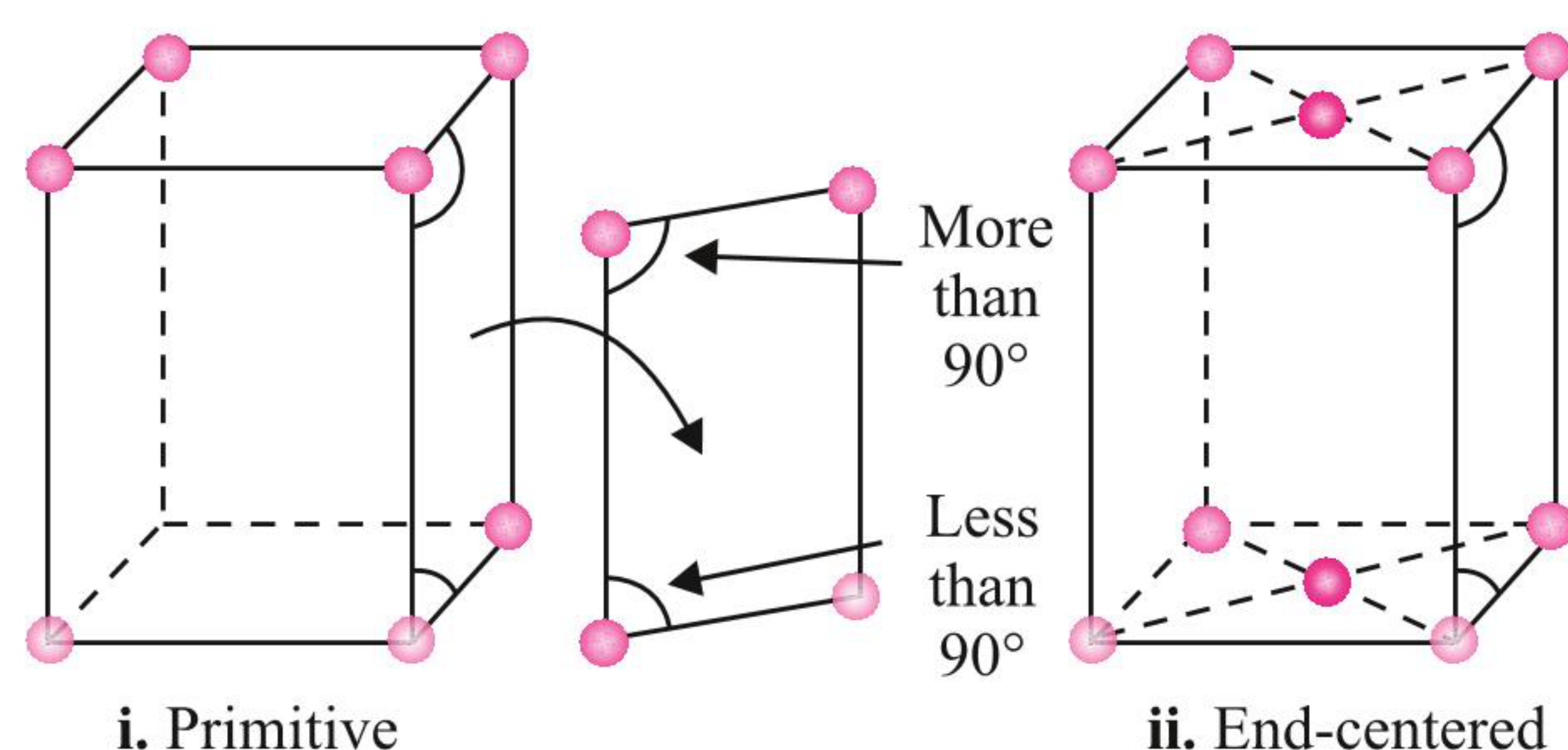


i. Primitive

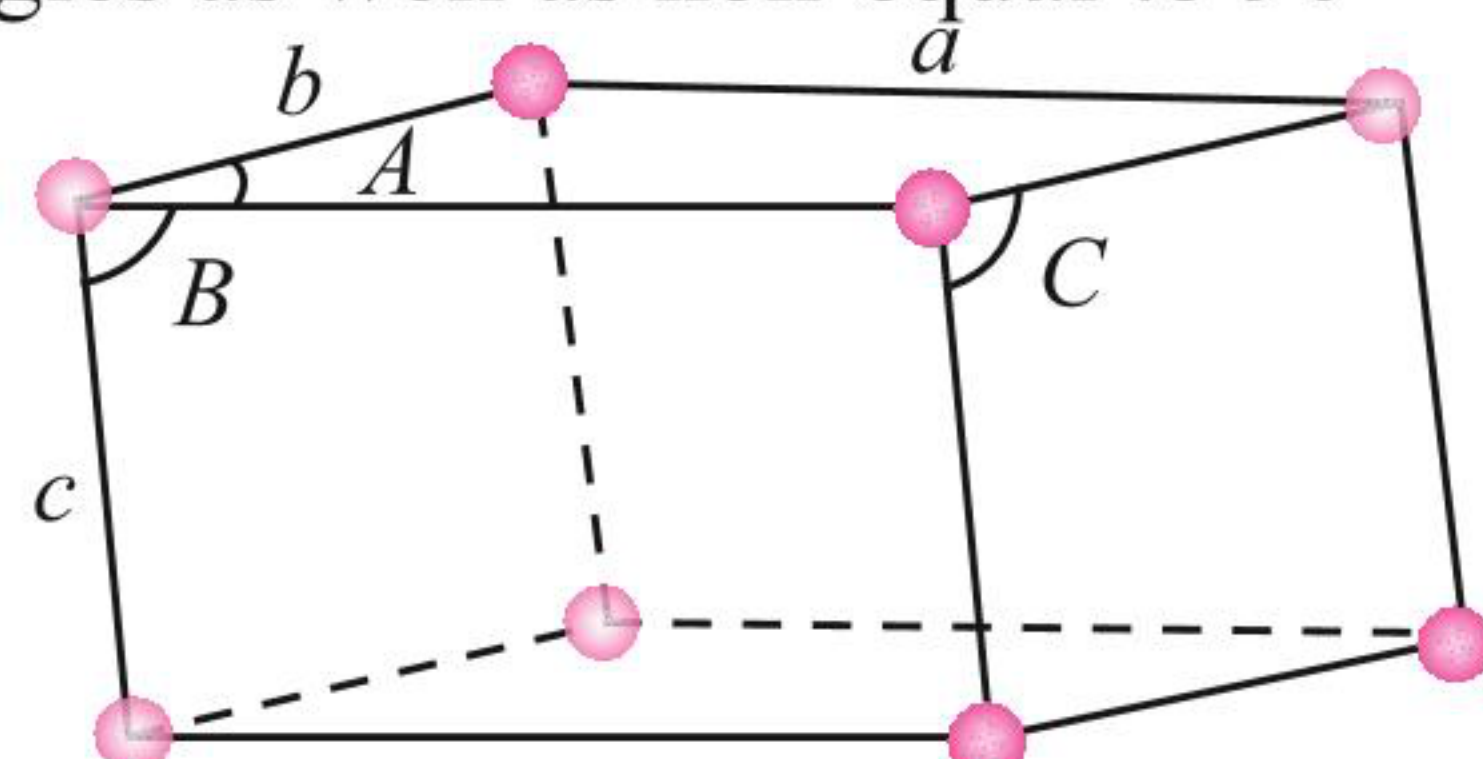


ii. Body-centered

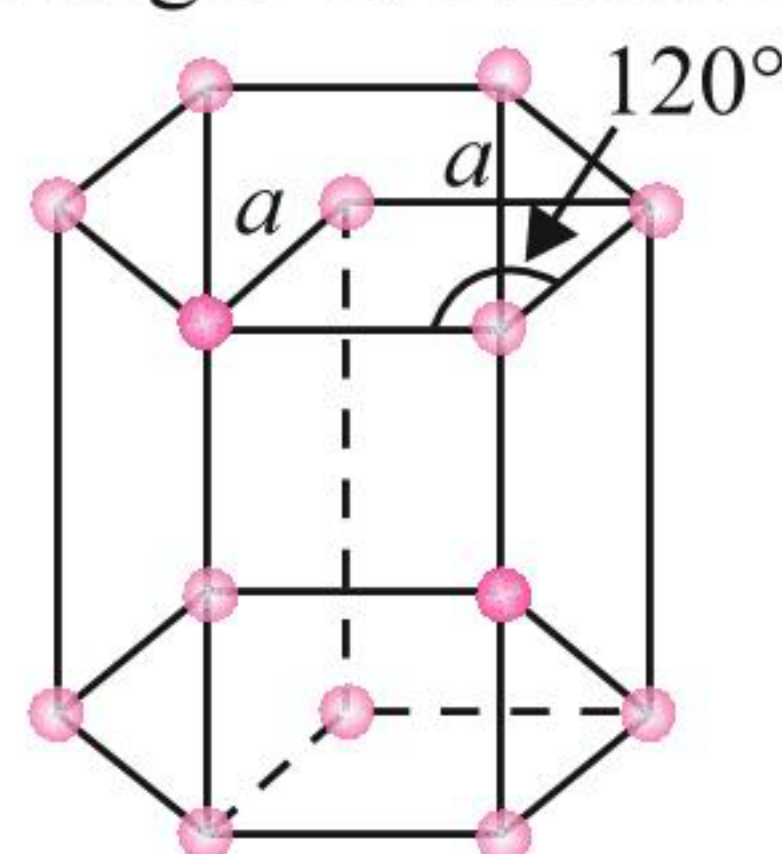
- 4. Monoclinic:** one side different in length to the other, only two angles between faces are 90°



- 5. Triclinic:** unequal sides a, b, c , and A, B, C are unequal angles as well as non-equal to 90°



- 6. Hexagonal:** one side different in length to the other two, the marked angle two faces are 120°



- 7. Rhombohedral:** All sides of equal length, only angles on two faces are 90°

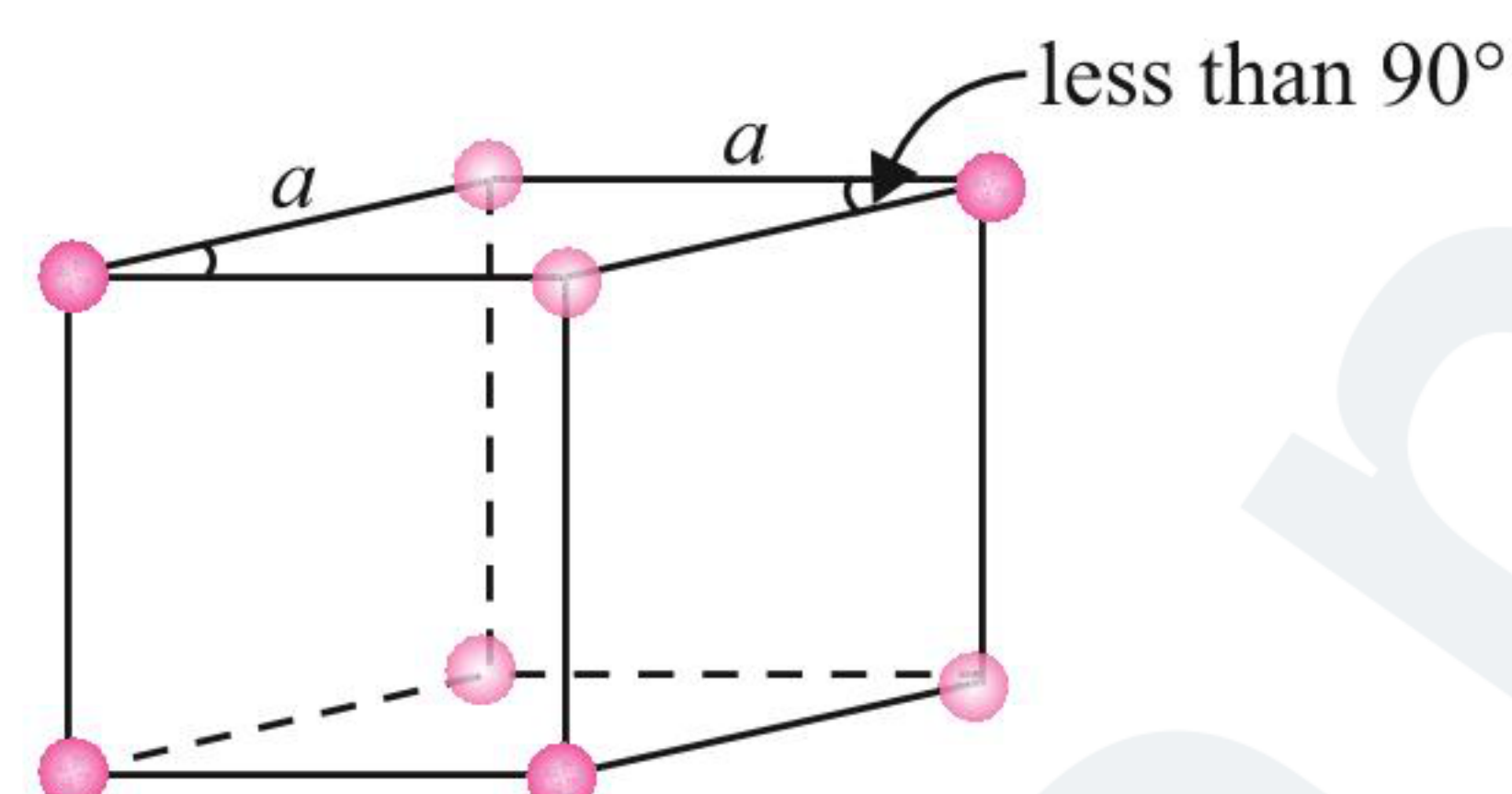


Fig. 1.21 Unit cells of 14 types of Bravais lattices

1.9 EFFECTIVE NUMBER OF ATOMS (Z_{eff}) IN A UNIT CELL

A crystal lattice is made up of a very large number of unit cells and every lattice point is occupied by one constituent particle (atom, molecule, or ion). In a crystal, a particular atom located at a particular corner/face centre of a unit cell is shared by other cells and only a portion of such an atom actually lies within a given unit cell. The sum of all such portions of the shared atoms present under one unit cell gives *effective number* (Z_{eff}) of atoms in a given unit cell.

Consider three types of cubic unit cells taking constituent particle as atom.

a. Primitive cubic unit cell

A primitive cubic unit cell has atoms only at its corner. Each atom at a corner is shared between eight adjacent unit cells as shown in Fig. 1.22, four unit cells in the same layer and

for unit cells of the upper (or lower) layer. Therefore, only $1/8$ th of an atom actually belongs to a particular unit cell. In Fig. 1.23, a primitive cubic unit cell has been shown in three different ways. Each small sphere in Fig. 1.23(a) represents only the centre of the particle occupying that position and not its actual size.

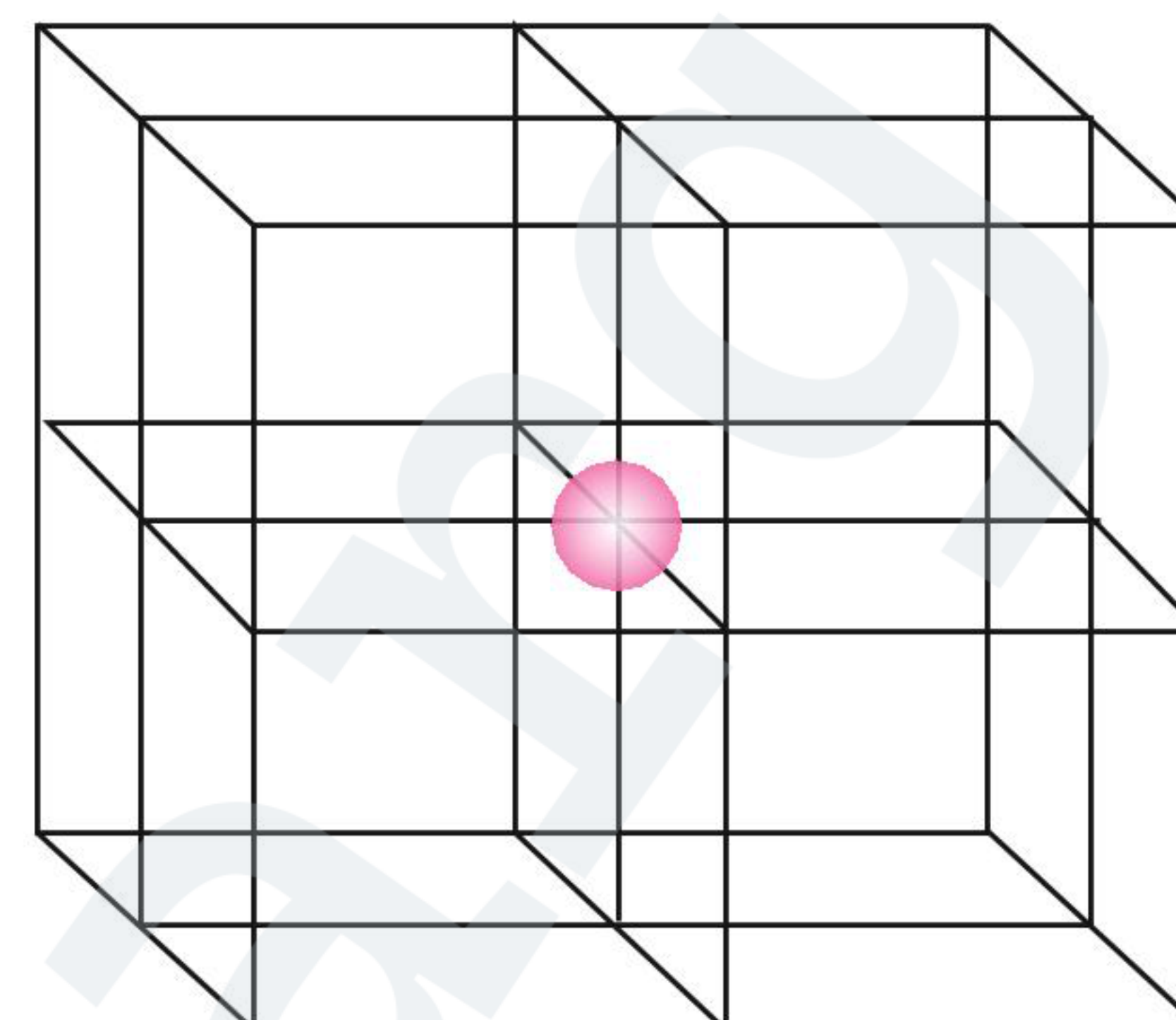


Fig. 1.22 In a simple cubic unit cell, each corner atom is shared between eight unit cells

Such structures are called open structures. The arrangement of particles is easier to follow in open structures. Figure 1.23(b) depicts the space-filling representation of a unit cell with actual particle size and Fig. 1.23(c) shows the actual portions of different atoms present in a cubic unit cell.

In all, since each cubic unit cell has 8 atoms on its corners, the total number of atoms in one unit cell is $8 \times \frac{1}{8} = 1$.

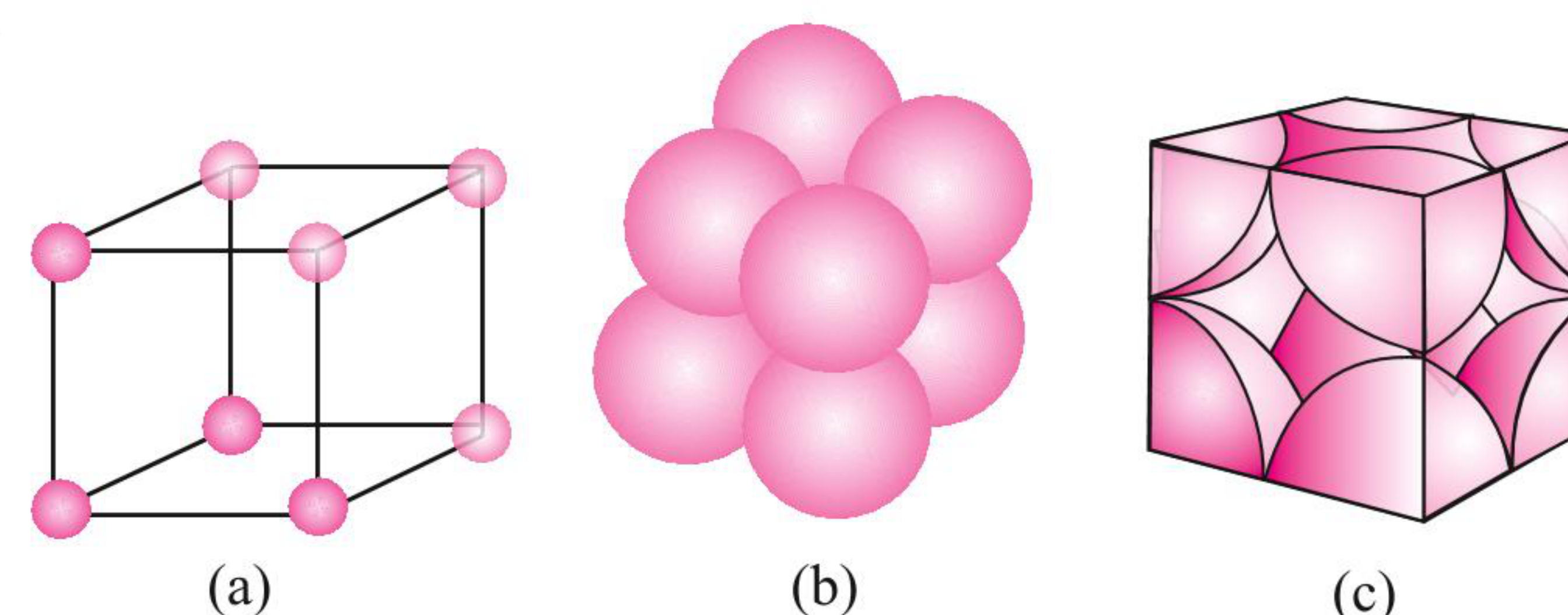
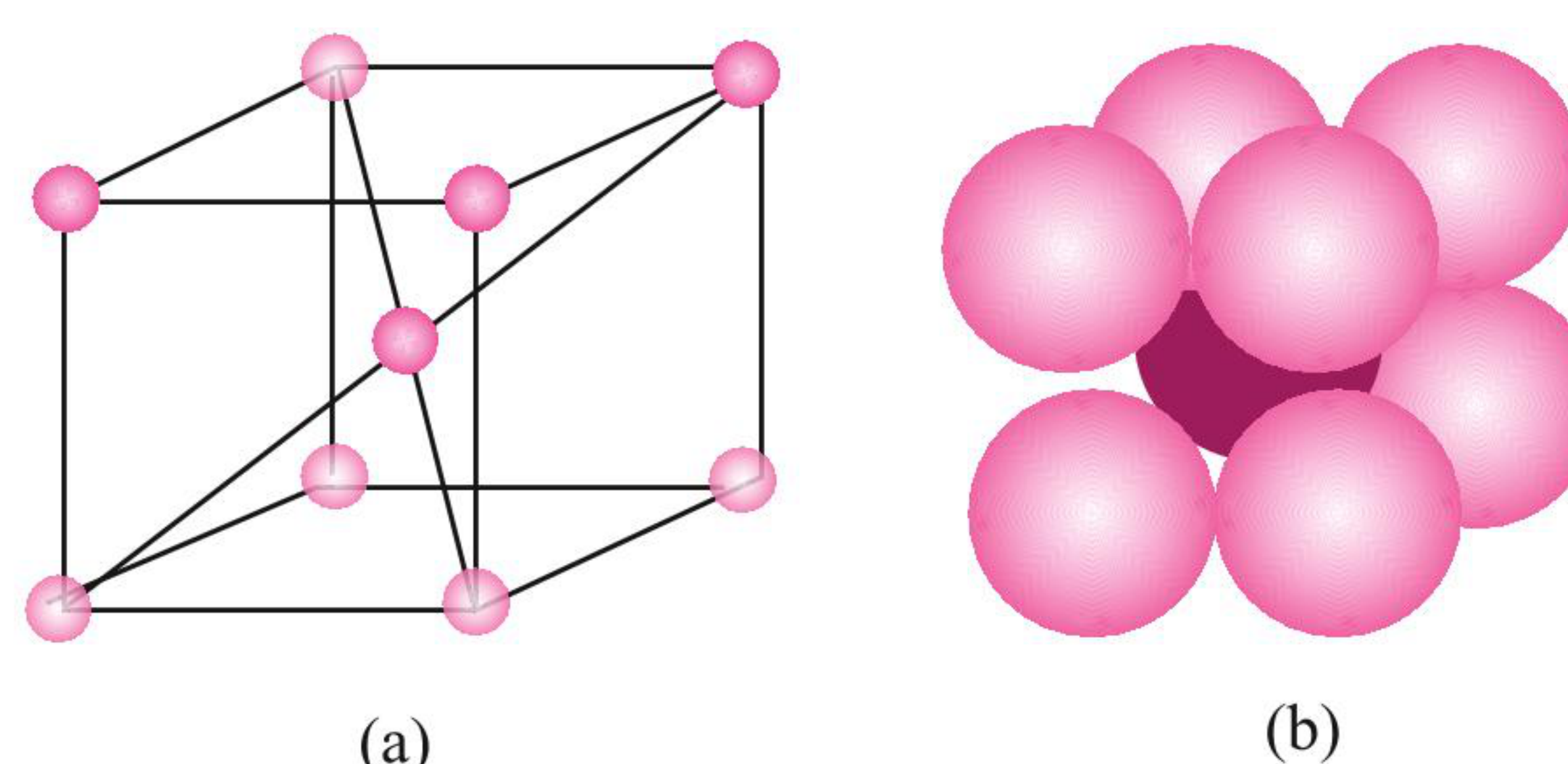


Fig. 1.23 A primitive cubic unit cell: (a) open structure, (b) space-filling structure, and (c) actual portions of atoms belonging to one unit cell

b. Body-centred cubic unit cell

A body-centred cubic (bcc) unit cell has an atom at each of its corners and also one atom at its body centre. Figure 1.24 depicts (a) open structure, (b) space filling model, and (c) the unit cell with portion of atoms actually belonging to it. It can be seen that the atom at the body centre wholly belongs to the unit cell in which it is present.



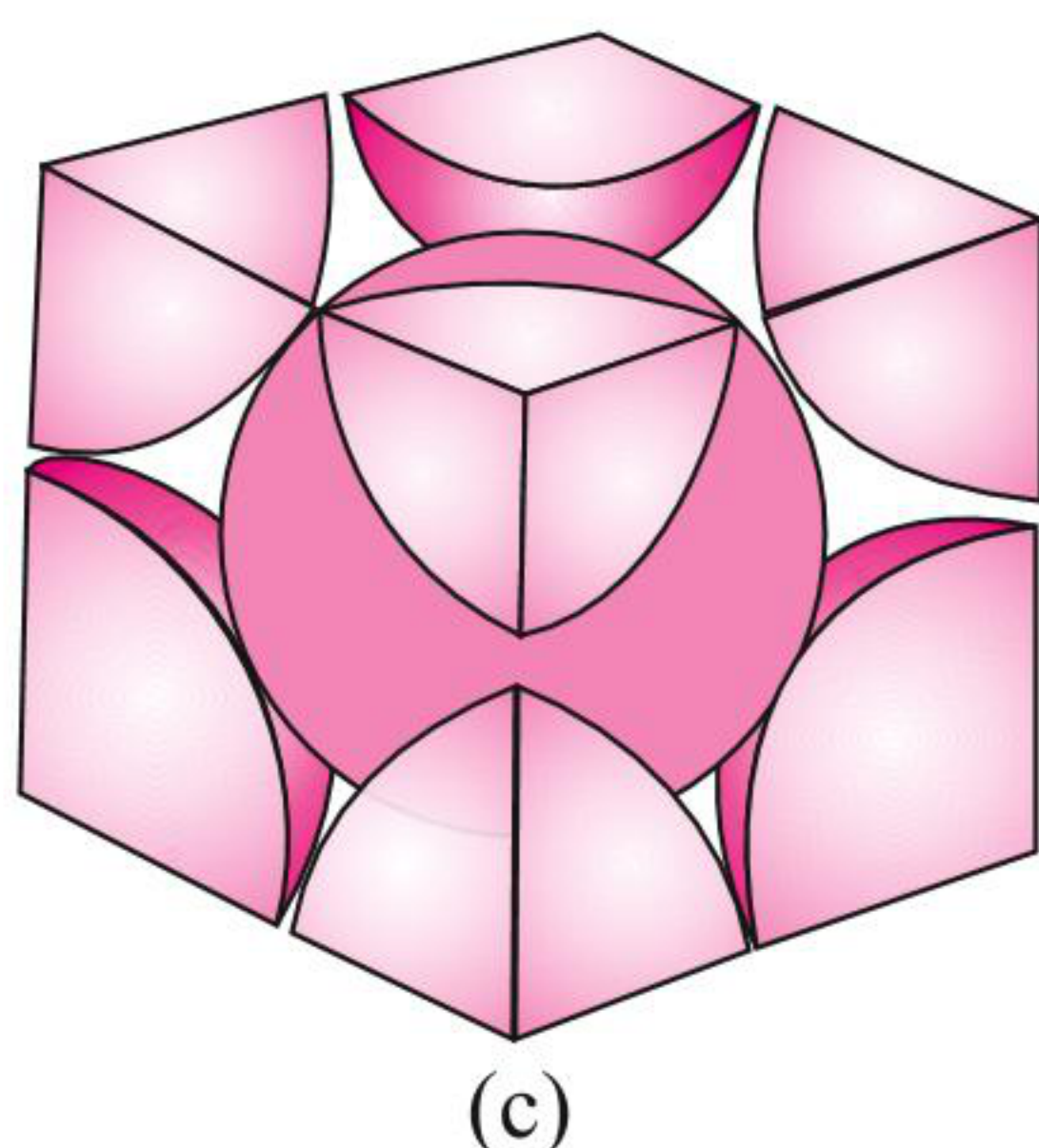


Fig. 1.24 A body-centred cubic unit cell: (a) open structure (b) space filling structure (c) actual portions of atoms belonging to one unit cell

Thus, in a body-centred cubic (bcc) unit cell:

- i. $8 \text{ corners} \times \frac{1}{8} \text{ per corner atoms} = 8 \times \frac{1}{8} = 1 \text{ atom}$
 - ii. $1 \text{ body centre atom} = 1 \times 1 = 1 \text{ atom}$
- $\therefore$ Total number of atoms per unit cell = 2 atoms

c. Face-centred cubic unit cell

A face-centred cubic (fcc) unit cell contains atoms at all the corners and at the centre of all the faces of the cube. It can be seen in Fig. 1.25(a) that each atom located at the face centre is shared between two adjacent unit cells and only half of each atom belongs to a unit cell. Figures 1.25(a)–1.25(d) depict open structure, space-filling model, and the unit cell with portions of atoms actually belonging to it, respectively.

Thus, in a face-centred cubic (fcc) unit cell:

- i. $8 \text{ corners atoms} \times \frac{1}{8} \text{ atoms/unit cell} = 8 \times \frac{1}{8} = 1 \text{ atom}$
- ii. $6 \text{ face-centred atoms} \times \frac{1}{2} \text{ atom/unit cell} = 6 \times \frac{1}{2} = 3 \text{ atoms}$

Total number of atom per unit cell = 4 atoms

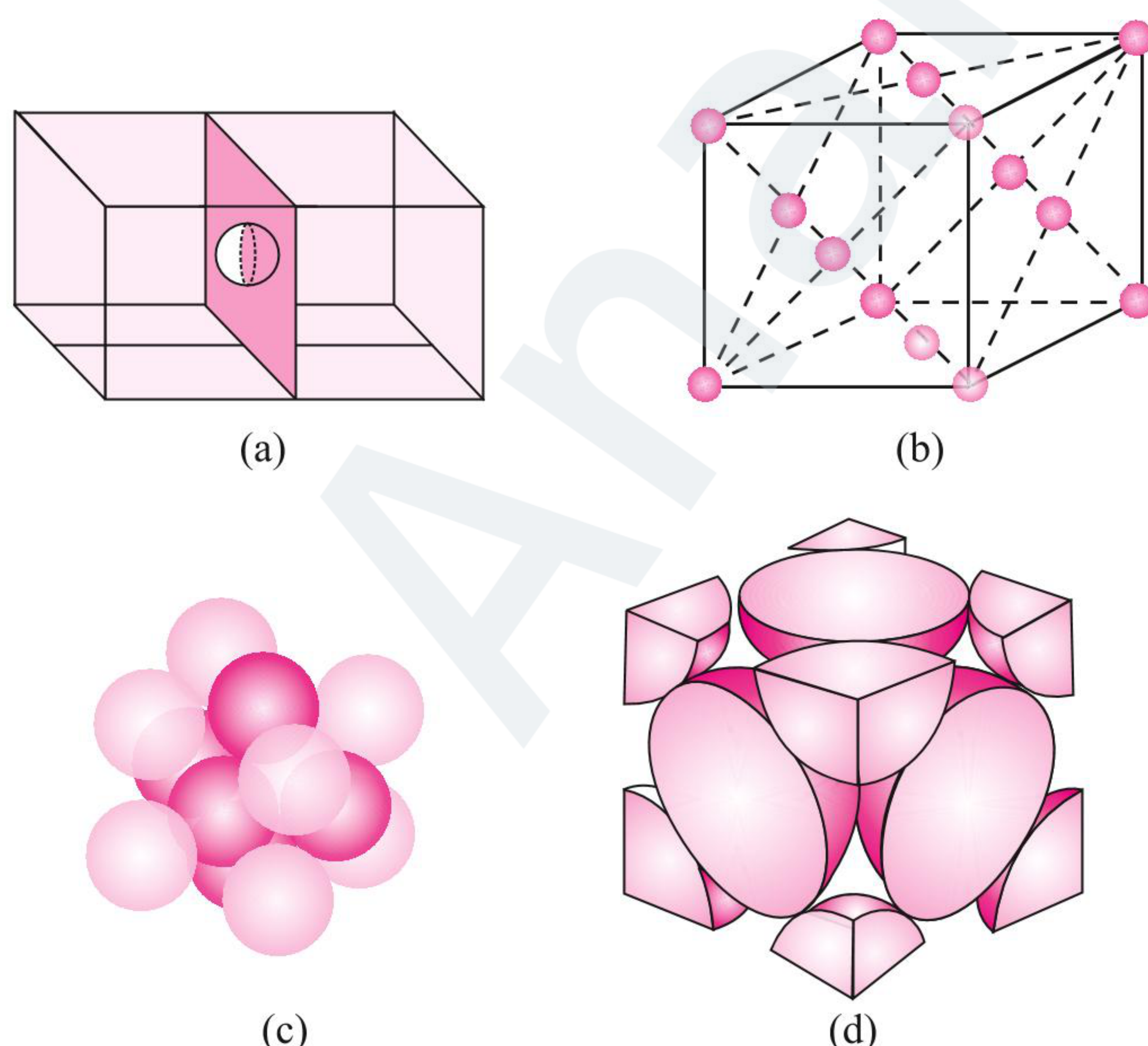


Fig. 1.25 A face-centred cubic unit cell: (a) An atom at face centre of unit cell is shared between two unit cells. (b) Open structure, (c) Space filling structure, (d) Actual portions of atoms belonging to one unit cells

d. Some other formulae

- i. Total number of atoms in a unit cell

$$= \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_b}{1} + \frac{n_e}{4}$$

where n_c = Number of atoms at the corners of a unit cell

n_f = Number of atoms at the centres of six faces of a unit cell

n_b = Number of atoms completely inside the body of a unit cell

n_e = Number of atoms at the edge centres of a unit cell

- ii. Number of effective atoms at the alternate faces of unit cell = $\frac{2}{2} = 1$

In a unit cell, there are only two alternate faces and each face-centred atom is shared between two unit cells and only half of each atom belongs to the unit cell.

$$\therefore 2 \text{ face-centred atoms} \times \frac{1}{2} \text{ atoms per unit cell} = 1 \text{ atom/unit cell.}$$

Such type of arrangement of atoms in a unit cell is called end-centred system [refer Fig. 1.19(d)].

- iii. Number of effective atoms at the alternate edge centres of unit cell = $4 \times \frac{1}{4} = 1$

In a unit cell, there are only four alternate edges and each edge-centred atom is shared between four unit cells and only 1/4th of each atom belongs to the unit cell (see Fig. 1.26).

$$\therefore 4 \text{ edge-centred atoms} \times \frac{1}{4} \text{ atoms per unit cell} = 1 \text{ atom/unit cell}$$

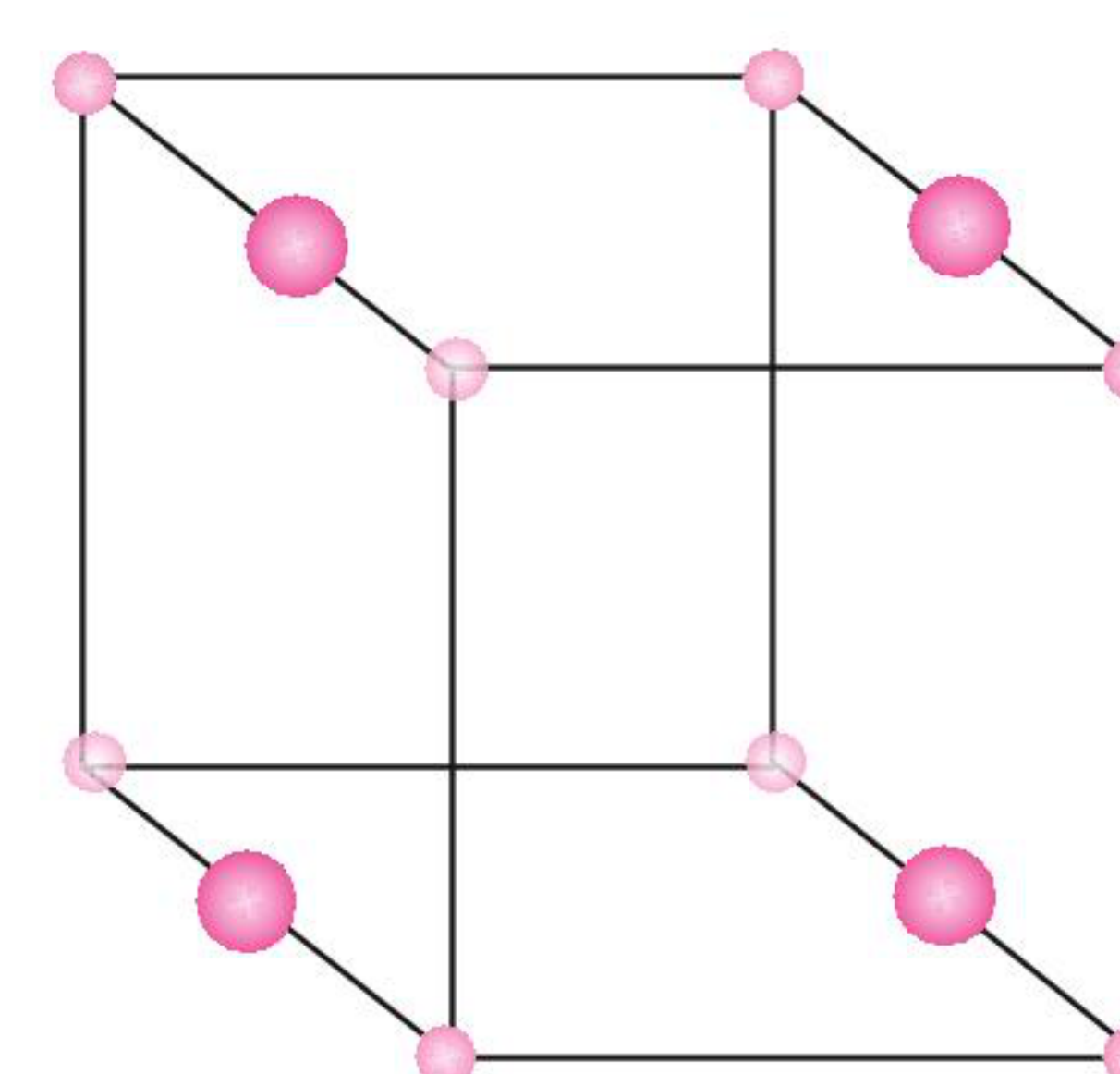


Fig. 1.26 Atoms at the alternative edge centres of a unit cell

- iv. Number of body diagonals of a unit cell = 4/unit cell
- Number of face diagonals of a unit cell = 2 diagonals on each face = $2 \times 6 \text{ faces} = 12/\text{unit cell}$

Note:

- a. Atoms on a body diagonal are inside the cube and they are not shared by any adjacent atoms.
- b. Atoms on a face diagonal are shared by two unit cells and only 1/2 of each atom belongs to each unit cell.

Table 1.4 Number of atoms (Z_{eff}) per unit cell

S. No.	Cubic unit cell	n_c	n_f	n_b	n_e	Effective atoms/unit cell
1.	Simple cubic (sc) or primitive	8	0	0	0	8 corners $\times \frac{1}{8}$ per corner atom share = 1 Total effective atoms = 1/unit cell
2.	Body-centred cubic (bcc)	8	0	1	0	Corner share = $\frac{1}{8} \times 8 = 1$ Body-centred share = 1 Total effective atoms = 1 + 1 = 2/unit cell
3.	Face-centred cubic (fcc)	8	6	0	0	Corner share = $\frac{1}{8} \times 8 = 1$ Face-centred share = $6 \times \frac{1}{2} = 3$ Total effective atoms = 1 + 3 = 4/unit cell

ILLUSTRATION 1.3

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and Y atoms are at the face centres.

- Calculate: (i) Z_{eff} , (ii) total number of atoms in a cube, and (iii) formula of the compound.
- If all the atoms are removed from a single axis passing through the centre of the cube, calculate (i) Z_{eff} , (ii) total number of atoms in a cube, and (iii) formula of the compound.

Sol.

- a. i.** Number of effective X atoms

$$= 8 \text{ corners} \times \frac{1}{8} \text{ per corner atom share}$$

$$= 1 \text{ atom/unit cell}$$

Number of effective Y atoms

$$= 8 \text{ corners} \times \frac{1}{2} \text{ per face atom share}$$

$$= 3 \text{ atom/unit cell}$$

$$Z_{\text{eff}}(8X + Y) = 1 + 3 = 4$$

- ii.** Total atoms in a cube

$$= 8X \text{ atoms at corner} + 6Y \text{ atoms at faces.}$$

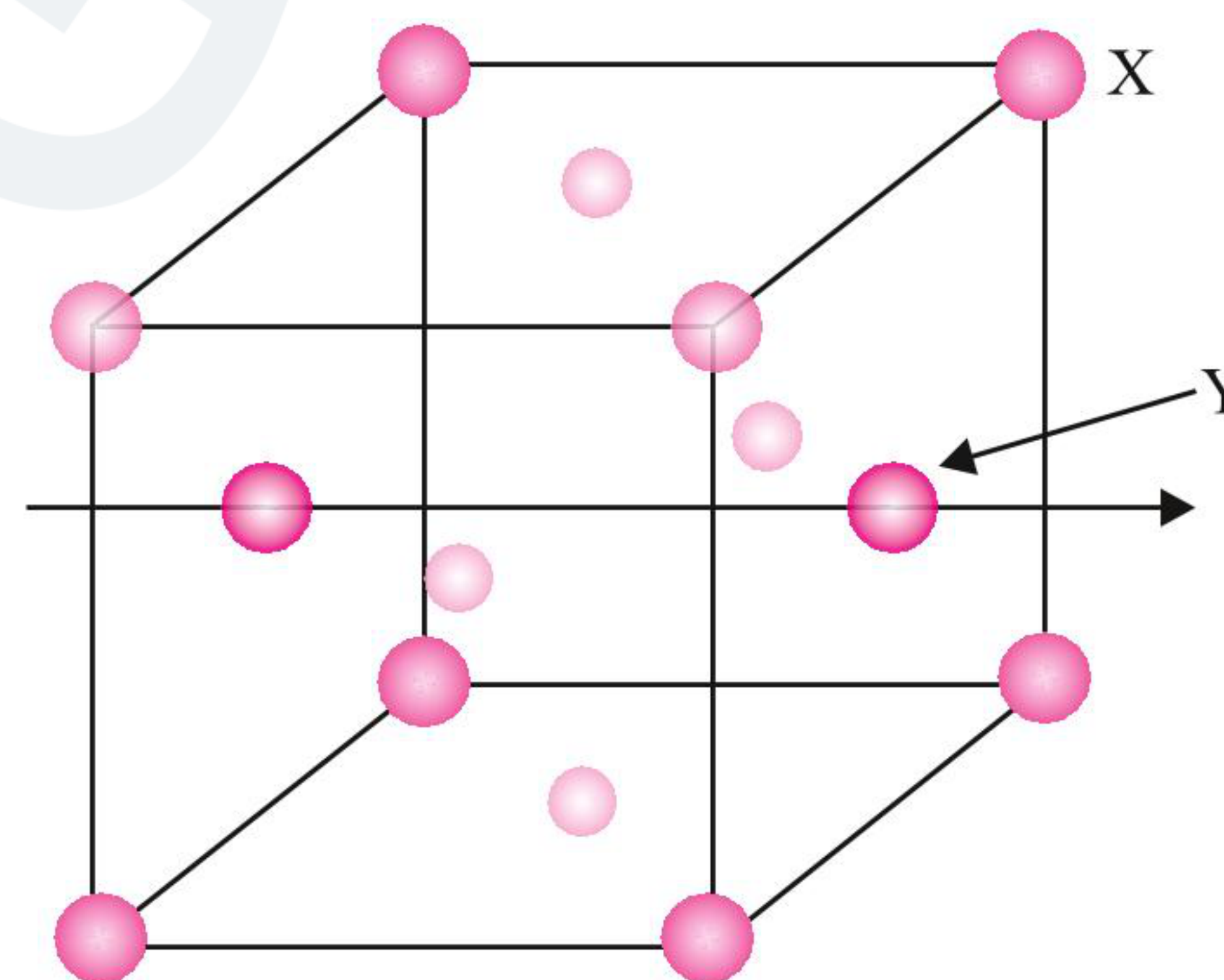
$$= 8 + 6 = 14 \text{ atoms/unit cube}$$

- iii.** Formula of the compound:

$$Z_{\text{eff}}(X) = 1, Z_{\text{eff}}(Y) = 3$$

Thus, formula of the compound = XY_3

- b. i.** Two atoms from two face centres are removed by passing an axis as shown in the figure below.



$$\therefore \text{Face centre atom left} = 6 - 2 = 4$$

$$Z_{\text{eff}}(Y) = 4 \text{ Face atom} \times \frac{1}{2} \text{ per face atom share} \\ = 2 \text{ atoms/unit cell}$$

$$Z_{\text{eff}}(X) = 8 \text{ corners} \times \frac{1}{8} \text{ per corner atom share} \\ = 1 \text{ atom/unit cell}$$

$$\therefore Z_{\text{eff}}(X + Y) = 2 + 1 = 3 \text{ atoms/unit cube.}$$

- ii.** Total atoms in a cube = 8 (corners) + 4 (face centre)
= 12 atoms/unit cube

- iii.** Formula of the compound:

$$Z_{\text{eff}}(X) = 1, Z_{\text{eff}}(Y) = 2$$

$$\therefore \text{Formula} = XY_2$$

ILLUSTRATION 1.4

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and two atoms (Y) are at each body diagonal of the cube.

- a. Calculate: (i) Z_{eff} , (ii) total number of atoms in a cube, and (iii) formula of the compound.
- b. If all atoms from one body diagonal of the cube except corners are removed, calculate: (i) Z_{eff} , (ii) total number of atoms in the cube, and (iii) formula of the compound.

Sol.

a. i. $Z_{\text{eff(X)}} \text{ at corners} = \frac{1}{8} \times 8 = 1 = X$

$$\begin{aligned} Z_{\text{eff(Y)}} \text{ at body diagonal} &= 2 \text{ atoms} \times 4 \text{ body diagonal} \\ &= 8 \text{ atoms/unit cell} \\ &= 8 = Y \end{aligned}$$

$$\therefore Z_{\text{eff(X+Y)}} = 1 + 8 = 9$$

Note: Body diagonal atoms are in the inner portion of the cubic unit cell and they are not shared with any adjacent atoms.

ii. Total atoms in a cube = 8 (corners) + 8 (body diagonal)

$$= 16 \text{ atoms/unit cube}$$

iii. Formula of the compound:

$$Z_{\text{eff(X)}} = 1, Z_{\text{eff(Y)}} = 8$$

$$\text{Formula} = \text{XY}_8$$

- b. i. One body diagonal has 2Y atoms and they are removed.

$$\therefore Z_{\text{eff(Y)}} \text{ at body diagonal left} = 8 - 2 = 6 \text{ atoms/unit cell}$$

$$Z_{\text{eff(X)}} \text{ at corners} = 8 \times \frac{1}{8} = 1 = X$$

$$\therefore Z_{\text{eff(X+Y)}} = 6 + 1 = 7 \text{ atoms/unit cell}$$

ii. Total atoms in a cube = 8 (corners) + 6 (body diagonal)

$$= 14 \text{ atoms/unit cube}$$

iii. Formula of the compound:

$$Z_{\text{eff(X)}} = 1, Z_{\text{eff(Y)}} = 6$$

$$\text{Formula: } \text{XY}_6$$

ILLUSTRATION 1.5

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and Y atoms are at the face centres. One atom X is missing from the corner.

- a. Calculate (i) Z_{eff} , (ii) total number of atoms in the cube, and (iii) formula of the compound.
- b. If all the atoms are removed from one of the faces of the cube containing atoms at corners, as in (a) above, calculate (i) Z_{eff} , (ii) total number of atoms in a cube, and (iii) formula of the compound.

Sol.

- a. i. Number of effective X atoms

$$= 7 \text{ corners} \times \frac{1}{8} \text{ per corner atom share}$$

$$= \frac{7}{8} \text{ atom/unit cell}$$

$$\begin{aligned} \text{Number of effective Y atoms} &= 6 \text{ faces} \times \frac{1}{2} \text{ per face atom share} \\ &= 3 \text{ atoms/unit cell} \end{aligned}$$

$$Z_{\text{eff(X+Y)}} = \frac{7}{8} + \frac{3}{1} = \frac{31}{8}$$

ii. Total atoms in a cube = 7 (corner) + 6 faces

$$= 13 \text{ atoms unit cube}$$

iii. Formula of the compound:

$$Z_{\text{eff(X)}} = \frac{7}{8}, Z_{\text{eff(Y)}} = 3$$

$$\text{Thus, formula of the compound is } \text{X}_{\frac{7}{8}}\text{Y}_3.$$

$$\text{Simplifying: } \text{X}_7\text{Y}_{24}.$$

- b. i. Atoms removed from one face of the cube, containing all atoms at corners = 4 corners + 1 face-centred atom
- $$= 5 \text{ atoms/unit cell}$$

$$\text{Corner atom left} = 7 - 4 = 3 \text{ atoms at corner}$$

$$\text{Face-centre atom left} = 6 - 1 = 5 \text{ atoms at face centre.}$$

$$\begin{aligned} Z_{\text{eff(X)}} &= 3 \text{ corner} \times \frac{1}{8} \text{ per corner atom share} \\ &= \frac{3}{8} \text{ atoms/unit cell} \end{aligned}$$

$$\begin{aligned} Z_{\text{eff(Y)}} &= 5 \text{ face-centred atom} \times \frac{1}{2} \text{ per face atom share} \\ &= \frac{5}{2} \text{ atoms/unit cell} \end{aligned}$$

ii. Total atoms in a cube = 3 (corner) + 5 (faces)

$$= 8 \text{ atoms/unit cube}$$

iii. Formula of compound:

$$Z_{\text{eff(X)}} = \frac{3}{8}, Z_{\text{eff(Y)}} = \frac{5}{2}.$$

$$\text{Formula: } \text{X}_{\frac{3}{8}}\text{Y}_{\frac{5}{2}}$$

$$\text{Simplifying} = \text{X}_3\text{Y}_{20}$$

ILLUSTRATION 1.6

A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and also at the face centres. Y atoms are present at the body centre and at the edge centre of the cube.

- a. Calculate (i) Z_{eff} , (ii) total number of atoms in the cube, and (iii) formula of the compound.

- b.** If all the atoms are removed from one of the body diagonals of the cube, calculate **(i)** Z_{eff} , **(ii)** total number of atoms in the cube, and **(iii)** formula of the compound.
- c.** If all the atoms from the diagonals of one of the face of the cube are removed, calculate **(i)** Z_{eff} , **(ii)** total number of atoms in the cube, and **(iii)** formula of the compound.
- d.** If all the atoms are removed from one of the plane passing through the middle of the cube, calculate **(i)** Z_{eff} , **(ii)** total number of atoms in the cube, and **(iii)** formula of the compound.
- e.** If all the atoms are removed from one of the axes passing through one of the face centres of the cube, calculate **(i)** Z_{eff} , **(ii)** total number of atoms in the cube, and **(iii)** formula of the compound.

Sol.

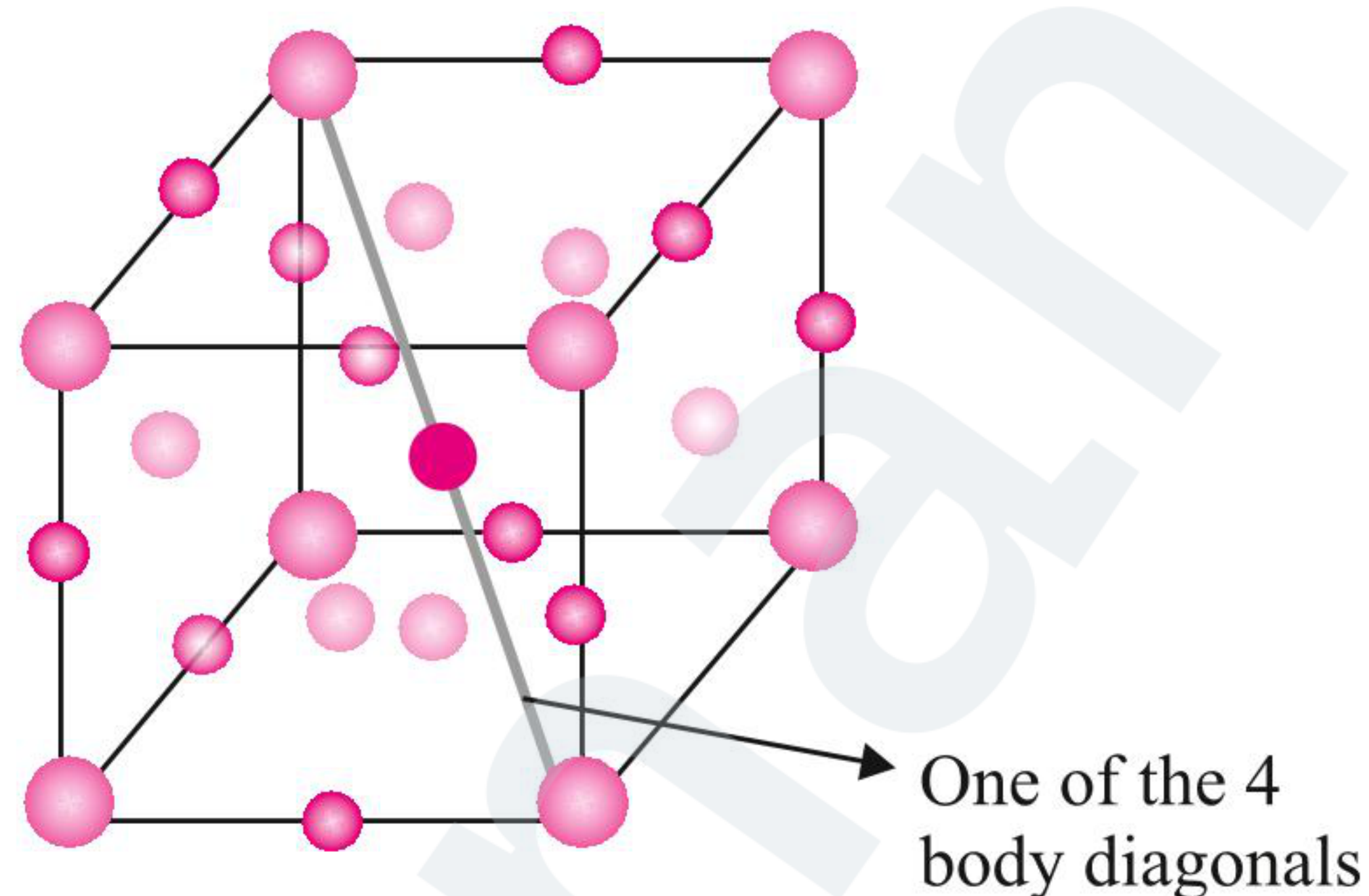
a. i. $Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{n_f}{2} = \frac{8}{8} + \frac{6}{2} = 1 + 3 = 4$

$$Z_{\text{eff}(Y)} = \frac{n_b}{8} + \frac{n_e}{4} = \frac{1}{8} + \frac{12}{4} = 1 + 3 = 4.$$

$$Z_{\text{eff}(X+Y)} = 4 + 4 = 8$$

- ii.** Total number of atoms in the cube
 = 8 (corner) + 6 (face centre) + 1 (body centre)
 + 12 (edge centre)
 = 27 atoms/unit cube

- iii.** Formula: $Z_{\text{eff}(X)} = 4$, $Z_{\text{eff}(Y)} = 4$
 $\Rightarrow X_4Y_4 = 4XY$

b. i.

$$X \Rightarrow \text{pink sphere} = 8 \text{ corner atoms}$$

$$Y \Rightarrow \text{dark pink sphere} = 1 \text{ body center atom}$$

$$Y \Rightarrow \text{light pink sphere} = 12 \text{ edge center atoms}$$

$$X \Rightarrow \text{light pink sphere} = 6 \text{ face center atoms}$$

Atoms removed from one body diagonal
 = 2 atoms from corner + 1 atom from body centre
 = 3 atoms.

$$Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{n_f}{2} = \frac{(8-2)}{8} + \frac{6}{2} = \frac{15}{4}$$

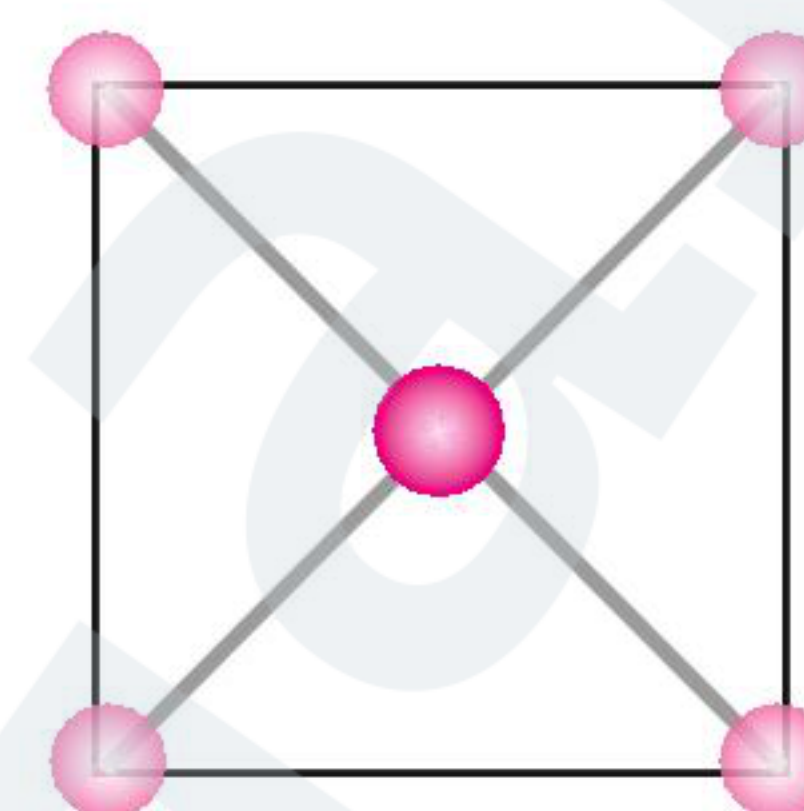
$$Z_{\text{eff}(Y)} = \frac{n_b}{8} + \frac{n_e}{4} = \frac{(1-1)}{8} + \frac{12}{4} = 0 + 3 = 3$$

$$Z_{\text{eff}(X+Y)} = \frac{15}{4} + 3 = \frac{27}{4}$$

- ii.** Total number of atoms in the cube
 = 6 (corner) + 6 (face centre) + Zero (body centre) + 12 (edge centre)
 = 24 atoms/unit cube

iii. $Z_{\text{eff}(X)} = \frac{15}{4}$, $Z_{\text{eff}(Y)} = 3$

$$\Rightarrow X_{\frac{15}{4}}Y_3.$$

Simplifying $X_{\frac{15}{4}}Y_{12}$ **c. i.**

$$X \Rightarrow \text{pink sphere} = 4 \text{ corner atoms are removed}$$

$$X \Rightarrow \text{dark pink sphere} = 1 \text{ face center atom is removed}$$

$$Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{n_f}{2} = \frac{(8-4)}{8} + \frac{(6-1)}{2} = \frac{1}{2} + \frac{5}{2} = 3$$

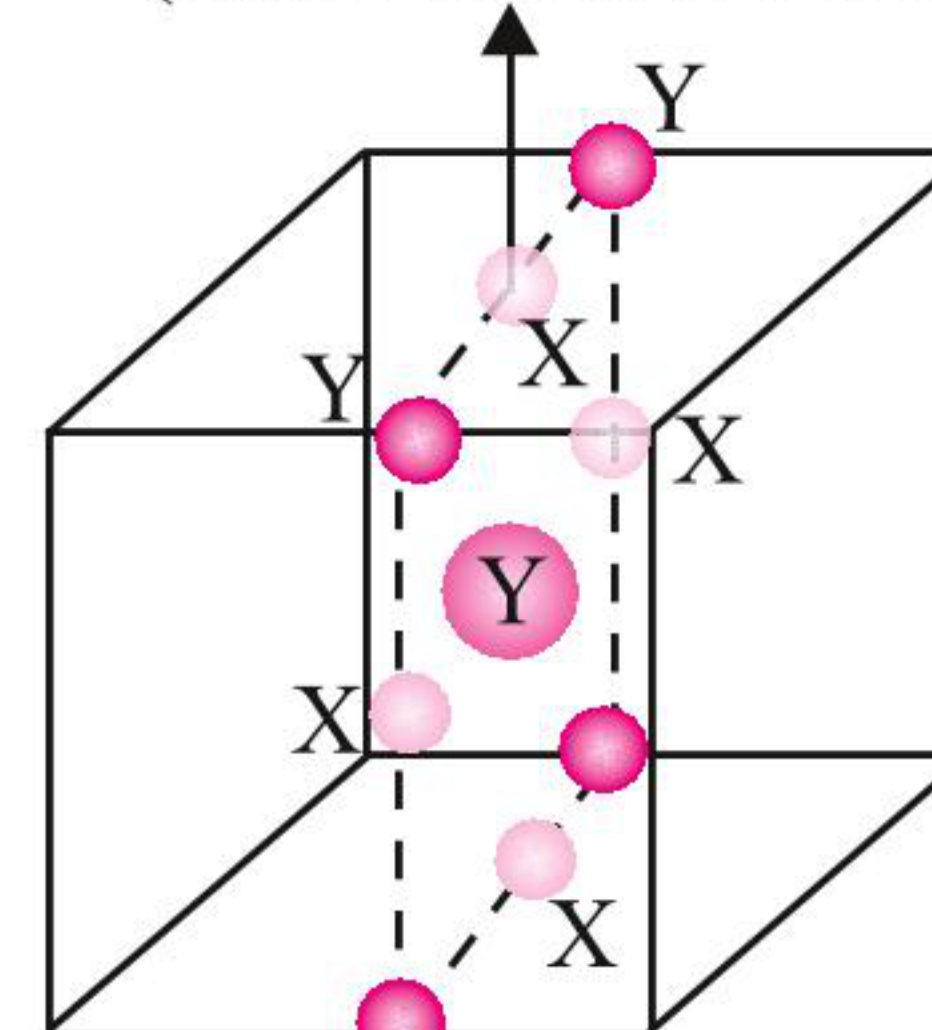
$$Z_{\text{eff}(Y)} = \frac{n_b}{8} + \frac{n_e}{4} = \frac{1}{8} + \frac{12}{4} = 1 + 3 = 4$$

$$Z_{\text{eff}(X+Y)} = 3 + 4 = 7$$

- ii.** Total number of atoms in a cube
 = 4 (corner) + 5 (face centre) + 1 (body centre)
 + 12 (edge centre)
 = 22 atoms/unit cube

- iii.** Formula: $Z_{\text{eff}(X)} = 3$, $Z_{\text{eff}(Y)} = 4$
 $\Rightarrow X_3Y_4.$

- d.** Plane passing through the middle of cube (other atoms are not shown)



$$Y \Rightarrow \text{dark pink sphere} = 1 \text{ body center atom is removed}$$

$$Y \Rightarrow \text{light pink sphere} = 4 \text{ edge center atoms are removed}$$

$$X \Rightarrow \text{light pink sphere} = 4 \text{ face center atoms are removed}$$

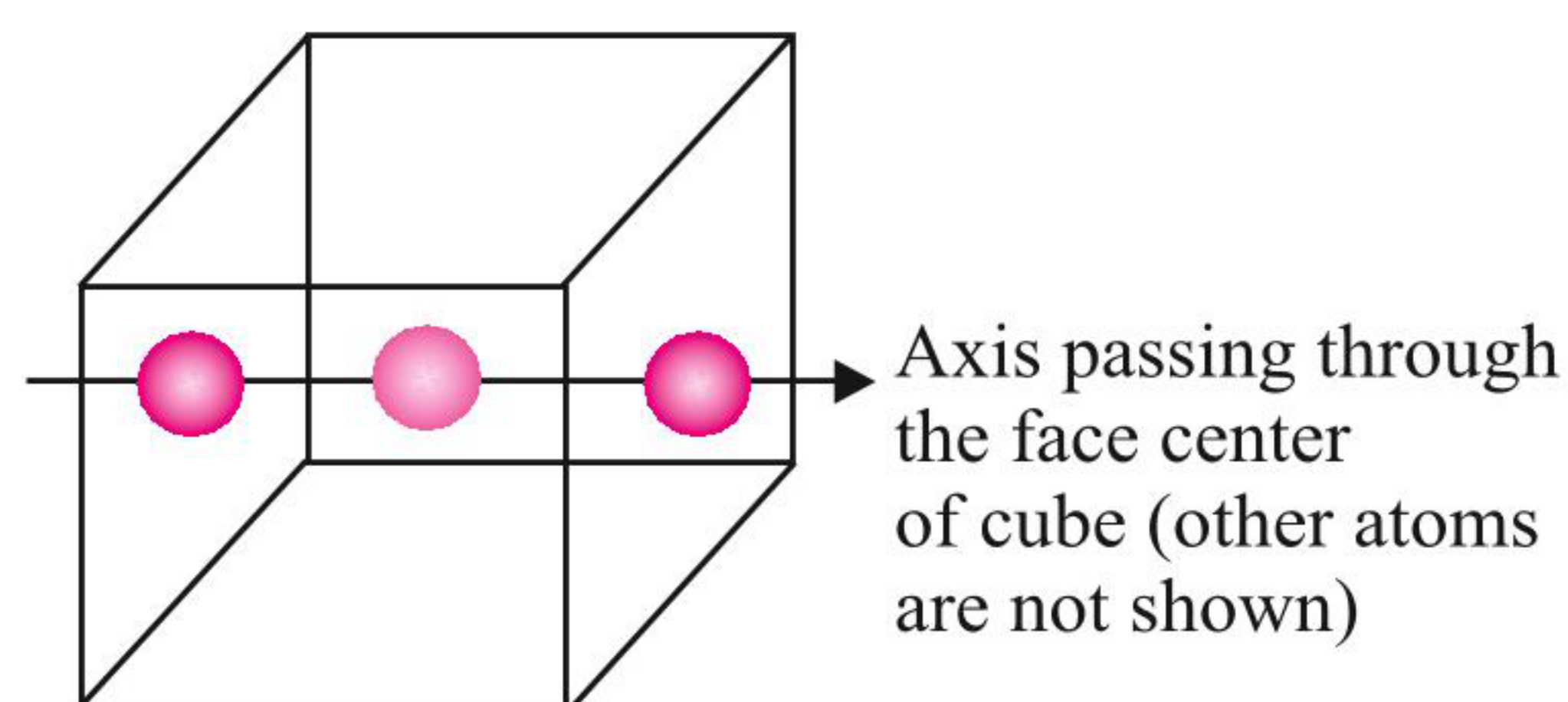
i. $Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{n_f}{2} = \frac{8}{8} + \frac{6-4}{2} = 1 + 1 = 2$

$$Z_{\text{eff}(Y)} = \frac{n_b}{8} + \frac{n_e}{4} = \frac{(1-1)}{8} + \frac{(12-4)}{4} = 2.$$

$$Z_{\text{eff}(X+Y)} = 2 + 2 = 4$$

- ii. Total number of atoms in the cube
 $= 8 \text{ (corner)} + 2 \text{ (face centres)} + \text{zero (body centre)} + 8 \text{ (edge centres)}$
 $= 18 \text{ atoms/unit cube}$
- iii. Formula: $Z_{\text{eff(X)}} = 2, Z_{\text{eff(Y)}} = 2$
 Formula is $X_2Y_2 = 2XY$.

e.



$Y \Rightarrow \text{pink circle} = 1 \text{ body center atom is removed}$

$X \Rightarrow \text{pink circle} = 2 \text{ face center atoms are removed}$

- i. $Z_{\text{eff(X)}} = \frac{n_c}{8} + \frac{n_f}{2} = \frac{8}{8} + \frac{(6-2)}{2} = 1 + 2 = 3.$
 $Z_{\text{eff(Y)}} = \frac{n_b}{8} + \frac{n_e}{4} = \frac{(1-1)}{1} + \frac{12}{4} = 0 + 3 = 3.$
 $Z_{\text{eff(X+Y)}} = 3 + 3 = 6.$
- ii. Total number atoms in a cube
 $= 8 \text{ (corner)} + 6 \text{ (face centre)}$
 $\text{zero (body centre)} + 12 \text{ (edge centre)}$
 $= 24 \text{ atoms/unit cube}$
- iii. Formula: $Z_{\text{eff(X)}} = 3, Z_{\text{eff(Y)}} = 3$
 Formula is X_3Y_3 or $3XY$.

ILLUSTRATION 1.7

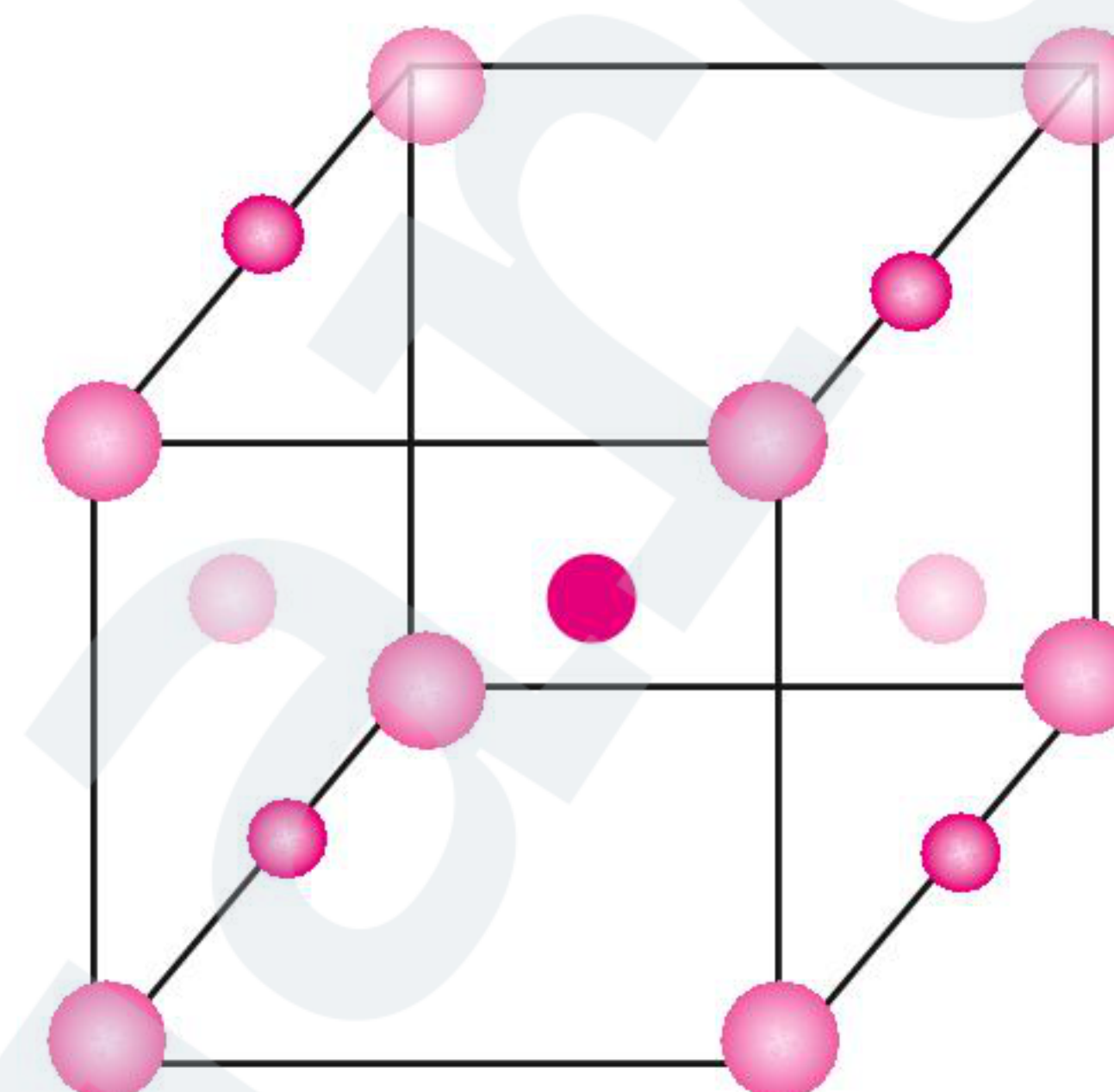
A compound formed by elements X and Y has a cubic structure in which X atoms are at the corner of the cube and also at alternate face centres. Y atoms are present at the body centre and also at the alternate edge centre of the cube.

- a. Calculate (i) Z_{eff} , (ii) total number of atoms in the cube, and (iii) formula of the compound.
- b. If all the atoms are removed from one of the plane passing through the middle of the cube which contains atoms both on the edge centre as well as on the face centre, calculate (i) Z_{eff} , (ii) total number of atoms in the cube, and (iii) formula of the compound.
- c. If all the atoms are removed from one of the plane passing through the middle of the cube which contains atoms only on the edge centre but not on face centre, calculate (i) Z_{eff} , (ii) total number of atoms in the cube, and (iii) formula of the compound.
- d. If all the atoms are removed from one of the plane passing through the middle of the cube which neither contains atoms on the edge centre nor on the face centre, calculate (i) Z_{eff} , (ii) total number of atoms in the cube, and (iii) formula of the compound.

- e. If all the atoms are removed from one of the axes passing through the middle of the cube containing face centre atoms, calculate (i) Z_{eff} , (ii) total number of atoms in a cube, and (iii) formula of the compound.
- f. If all the atoms are removed from one of the axes passing through the middle of the cube not containing face centre atoms, calculate (i) Z_{eff} , (ii) total number of atoms in the cube, and (iii) formula of the compound.

Sol.

a. i.



$X \Rightarrow \text{pink circle} = 8 \text{ corner atoms}$

$X \Rightarrow \text{pink circle} = 2 \text{ alternate face center atoms}$

$Y \Rightarrow \text{pink circle} = 4 \text{ alternate edge center atoms}$

$Y \Rightarrow \text{pink circle} = 1 \text{ body center atom}$

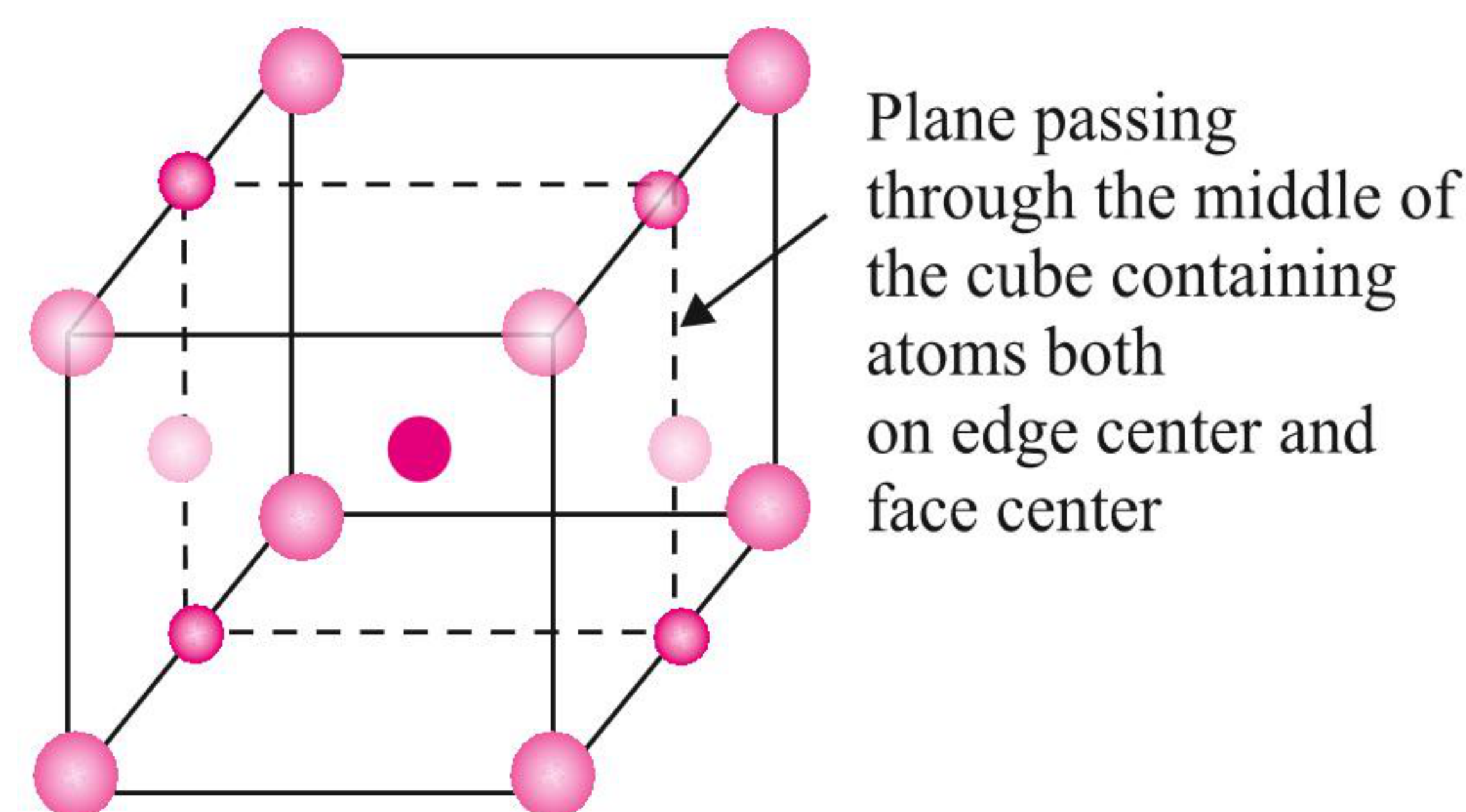
$$Z_{\text{eff(X)}} = \frac{n_c}{8} + \frac{\text{Alternate } n_f}{2} = \frac{8}{8} + \frac{2}{2} = 1 + 1 = 2$$

$$Z_{\text{eff(Y)}} = \frac{n_b}{1} + \frac{\text{Alternate } n_e}{4} = \frac{1}{1} + \frac{4}{4} = 1 + 1 = 2$$

$$Z_{\text{eff(X+Y)}} = 2 + 2 = 4$$

- ii. Total number of atoms in a cube
 $= 8 \text{ (corner)} + 2 \text{ (alternate face centre)}$
 $+ 4 \text{ (alternate edge centre)} + 1 \text{ (body centre)}$
 $= 15 \text{ atoms/unit cube}$
- iii. Formula: $Z_{\text{eff(X)}} = 2, Z_{\text{eff(Y)}} = 2$
 $\therefore \text{Formula} = X_2Y_2 = 2XY$

b. i.



$X \Rightarrow \text{pink circle} = 2 \text{ X atoms from face center are removed}$

$Y \Rightarrow \text{pink circle} = 4 \text{ Y atoms from edge center are removed}$

$Y \Rightarrow \text{pink circle} = 1 \text{ Y atom from body center is removed}$

$$Z_{\text{eff(X)}} = \frac{n_c}{8} + \frac{\text{Alternate } n_f}{2} = \frac{8}{8} + \frac{(2-2)}{2} = 1 + 0 = 1$$

$$Z_{\text{eff}(Y)} = \frac{n_b}{1} + \frac{\text{Alternate } n_e}{4} = \frac{(1-1)}{1} + \frac{(4-4)}{4} = 0 + 0 = \text{zero}$$

$$Z_{\text{eff}(X+Y)} = 1 + 0 = 1$$

ii. Total number of atoms in a cube

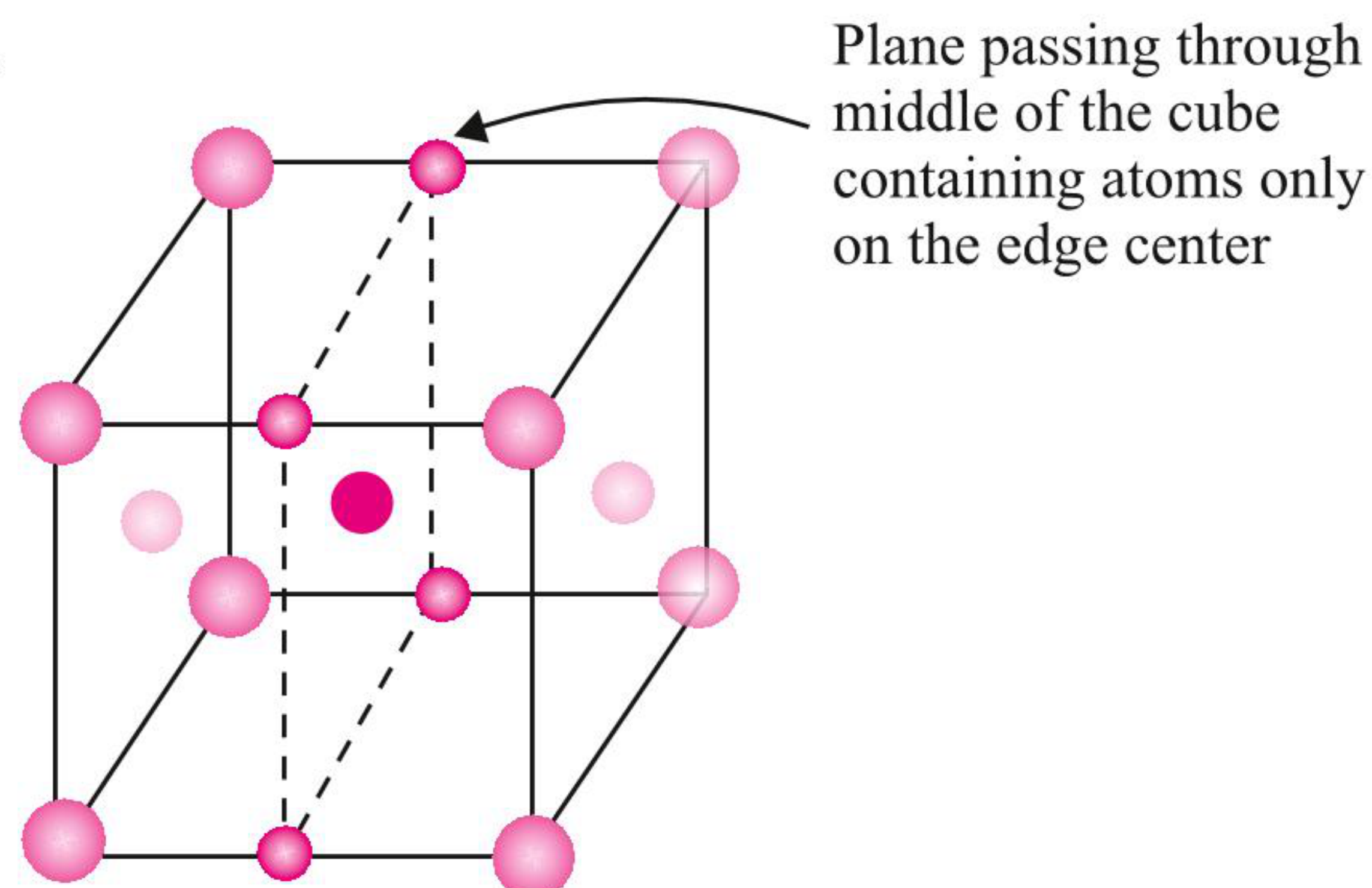
= 8 (corner) + zero (body centre) + zero (face centre) + zero (edge centre)

= 8 atoms/unit cube

iii. Formula: $Z_{\text{eff}(X)} = 1$, $Z_{\text{eff}(Y)} = \text{zero}$

$\therefore$ Formula = X

c. i.



$Y \Rightarrow \bullet = 4$ Y atoms from edge center are removed

$Y \Rightarrow \bullet = 1$ Y atom from body center is removed

$$\therefore Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{n_f (\text{Alternate})}{2} = \frac{8}{8} + \frac{2}{2} = 1 + 1 = 2$$

$$Z_{\text{eff}(Y)} = \frac{n_b}{1} + \frac{n_e (\text{Alternate})}{4} = \frac{(1-1)}{1} + \frac{(4-4)}{4} = 0 + 0 = 0$$

$$Z_{\text{eff}(X+Y)} = 2 + 0 = 2$$

ii. Total number of atoms in a cube

= 8 (corner) + 2 (alternate face centre)

+ zero (body centre)

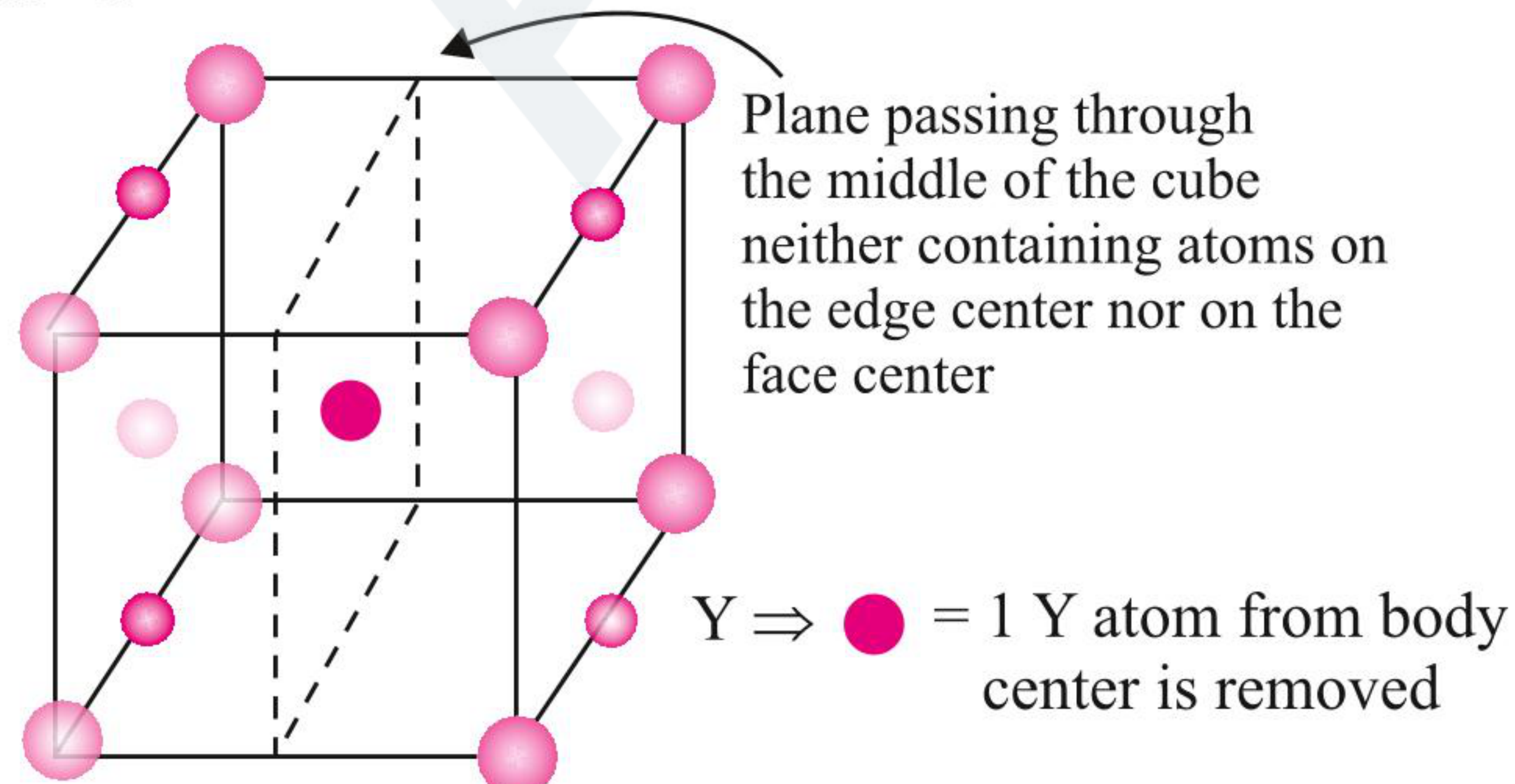
+ zero (alternate edge centre)

= 10 atoms/unit cube

iii. Formula: $Z_{\text{eff}(X)} = 2$, $Z_{\text{eff}(Y)} = \text{Zero}$

Formula = X_2

d. i.



$$\therefore Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{(\text{Alternate}) n_f}{2} = \frac{8}{8} + \frac{2}{2} = 1 + 1 = 2$$

$$Z_{\text{eff}(Y)} = \frac{n_b}{1} + \frac{(\text{Alternate}) n_e}{4} = \frac{(1-1)}{1} + \frac{(4)}{4} = 0 + 1 = 1$$

$$Z_{\text{eff}(X+Y)} = 2 + 1 = 3.$$

ii. Total number of atoms in a cube

= 8 (corner) + 2 (alternate face centre)

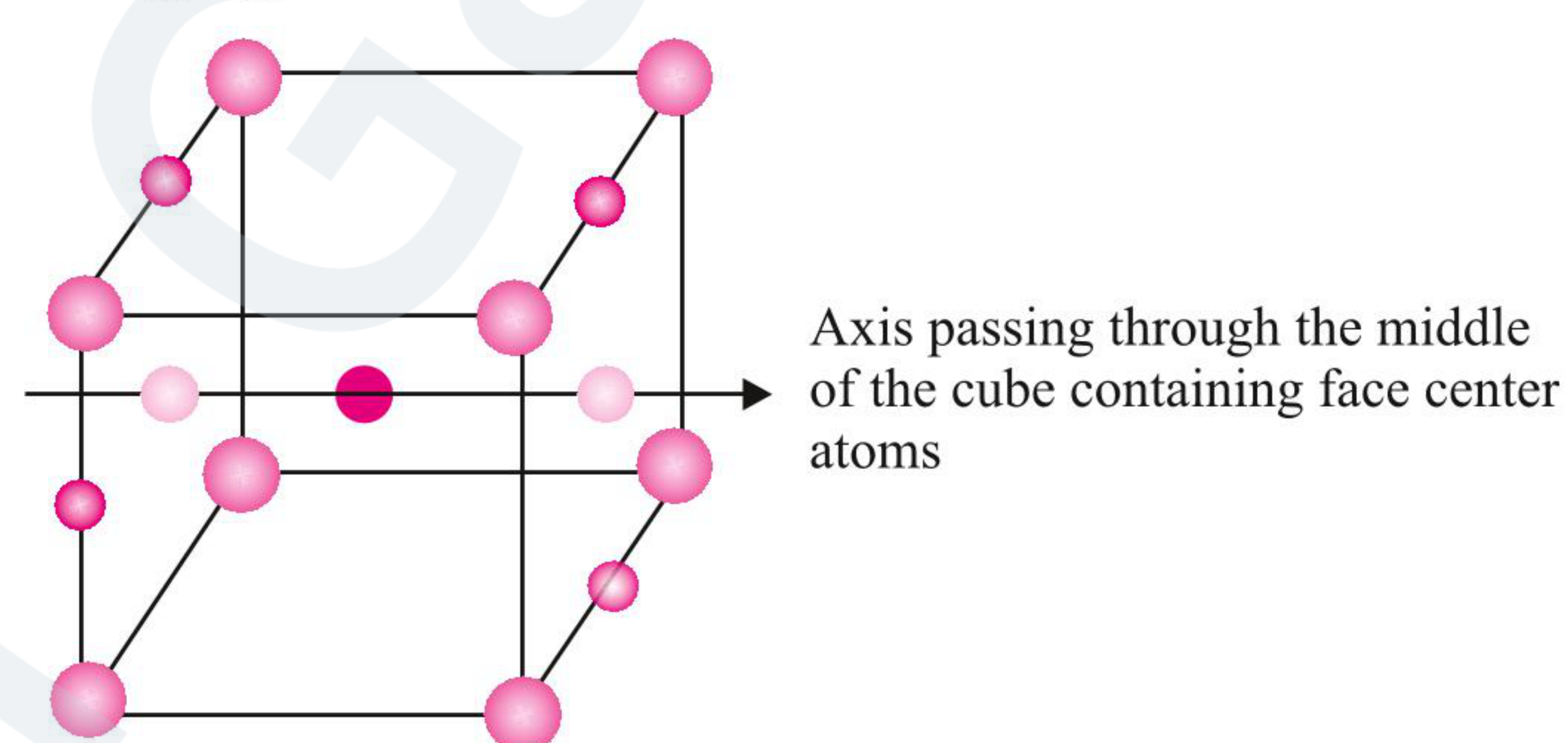
+ 4 (alternate edge centre) + zero (body centre)

= 14 atoms/unit cube

iii. Formula: $Z_{\text{eff}(X)} = 2$, $Z_{\text{eff}(Y)} = 1$

$\therefore$ Formula = X_2Y

e. i.



$Y \Rightarrow \bullet = 1$ Y atom from body center is removed

$X \Rightarrow \bullet = 2$ X atoms from face center are removed

$$\therefore Z_{\text{eff}(X)} = \frac{n_c}{8} + \frac{\text{Alternate } n_f}{2} = \frac{8}{8} + \frac{(2-2)}{2} = 1 + 0 = 1$$

$$Z_{\text{eff}(Y)} = \frac{n_b}{1} + \frac{\text{alternate } (n_e)}{4} = \frac{(1-1)}{1} + \frac{4}{4} = 0 + 1 = 1$$

$$Z_{\text{eff}(X+Y)} = 1 + 1 = 2$$

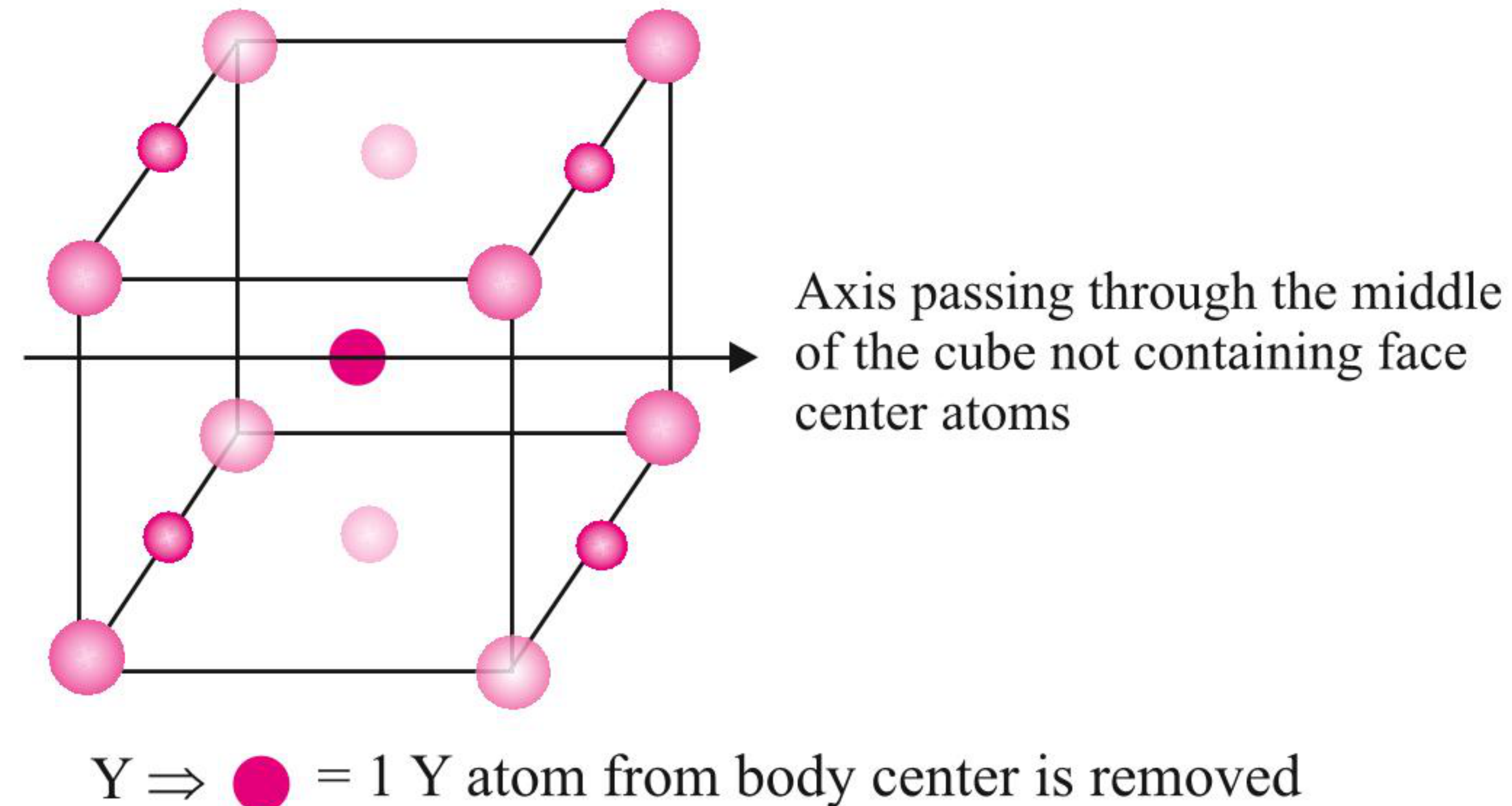
ii. Total number of atoms in a cube

= 8 (corner) + 4 (edge centre) + zero (body centre) + zero (face centre) = 12 atoms/unit cube.

iii. Formula: $Z_{\text{eff}(X)} = 1$, $Z_{\text{eff}(Y)} = 1$.

$\therefore$ Formula = XY.

f. i.



$$\therefore Z_{\text{eff(X)}} = \frac{n_c}{8} + \frac{\text{Alternate } n_f}{2} = \frac{8}{8} + \frac{2}{2} = 1 + 1 = 2$$

$$Z_{\text{eff(Y)}} = \frac{n_b}{1} + \frac{\text{Alternate } n_e}{4} = \frac{(1-1)}{1} + \frac{4}{4} = 0 + 1 = 1$$

$$Z_{\text{eff(X+Y)}} = 2 + 1 = 3$$

ii. Total number of atoms in a cube

$$= 8 \text{ (corner)} + 2 \text{ (face centre)}$$

$$+ 4 \text{ (edge centre)} + \text{zero (body centre)}$$

$$= 14 \text{ atoms/unit cube}$$

iii. Formula: $Z_{\text{eff(X)}} = 2$, $Z_{\text{eff(Y)}} = 1$

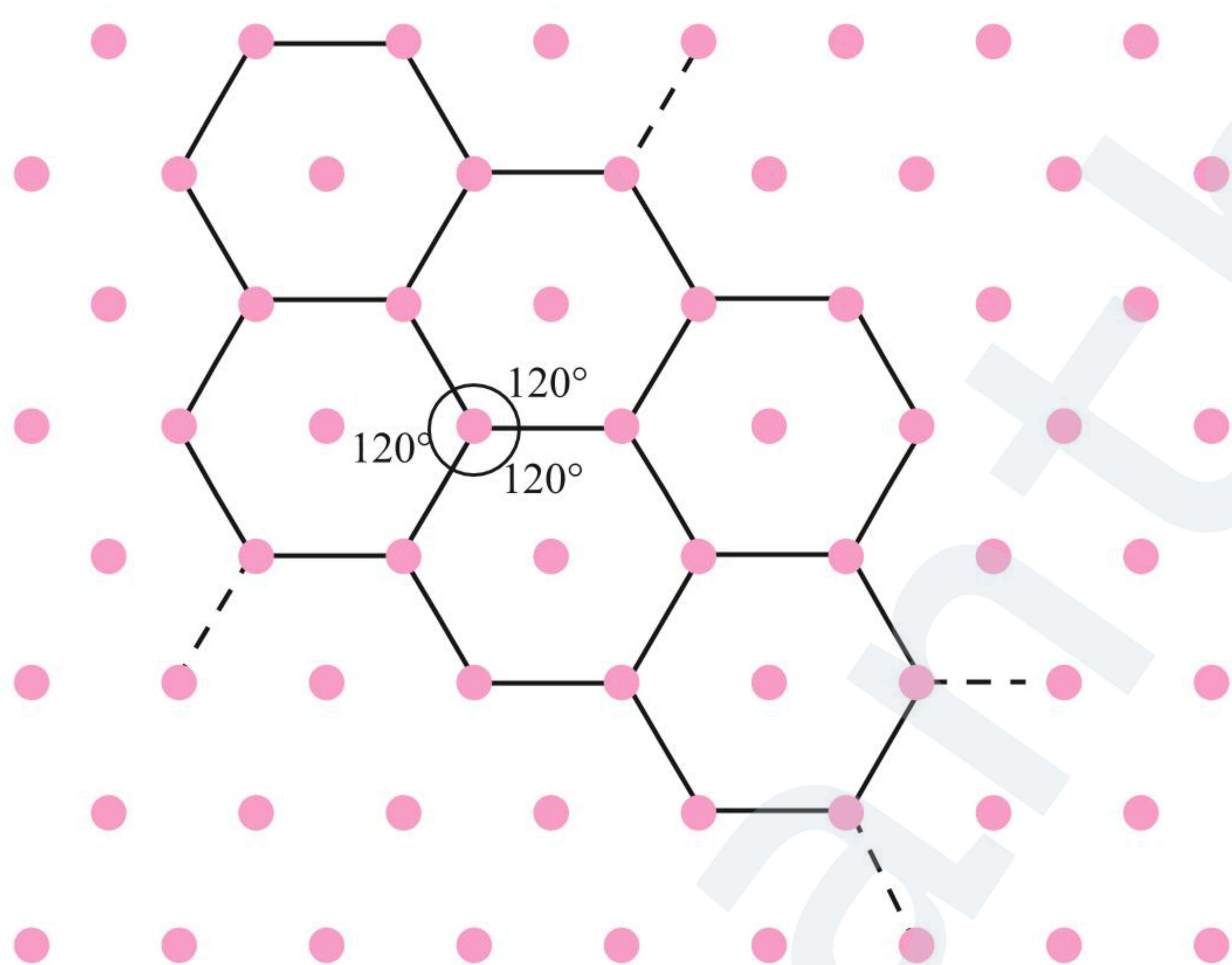
$$\therefore \text{Formula} = \text{X}_2\text{Y}$$

ILLUSTRATION 1.8

Draw a two-dimensional hexagonal lattice. Try to visualize the possibility of pentagonal two-dimensional lattice.

Sol.

Three regular hexagons intersect at one point. So, in this two-dimensional lattice, this lattice point is shared by three unit cells.



So, the effective number of lattice points per unit cell
 $= 6 \times \left(\frac{1}{3}\right) + 1 \times (1) = 3$.

A regular pentagon has an interior angle of 108° . As 360° is not an integral multiple of 108° , pentagons cannot be made to meet at a point bearing a constant angle to one another. Hence, a pentagonal lattice is not possible. On the other hand, a square or a hexagonal two-dimensional lattice is possible as their internal angles add up to give 360° .

1.10 ATOMIC RADIUS AND SHORTEST DISTANCES IN CUBIC SYSTEM

The atomic radius is defined as half the distance (centre to centre) between the neighbouring atoms in a crystal. It is expressed in terms of edge a of the unit cell of a crystal.

a. Simple cubic (sc)

Each corner atom is in contact with its corner atoms as in Fig. 1.27.

$$2r = a \Rightarrow r = \frac{a}{2}$$

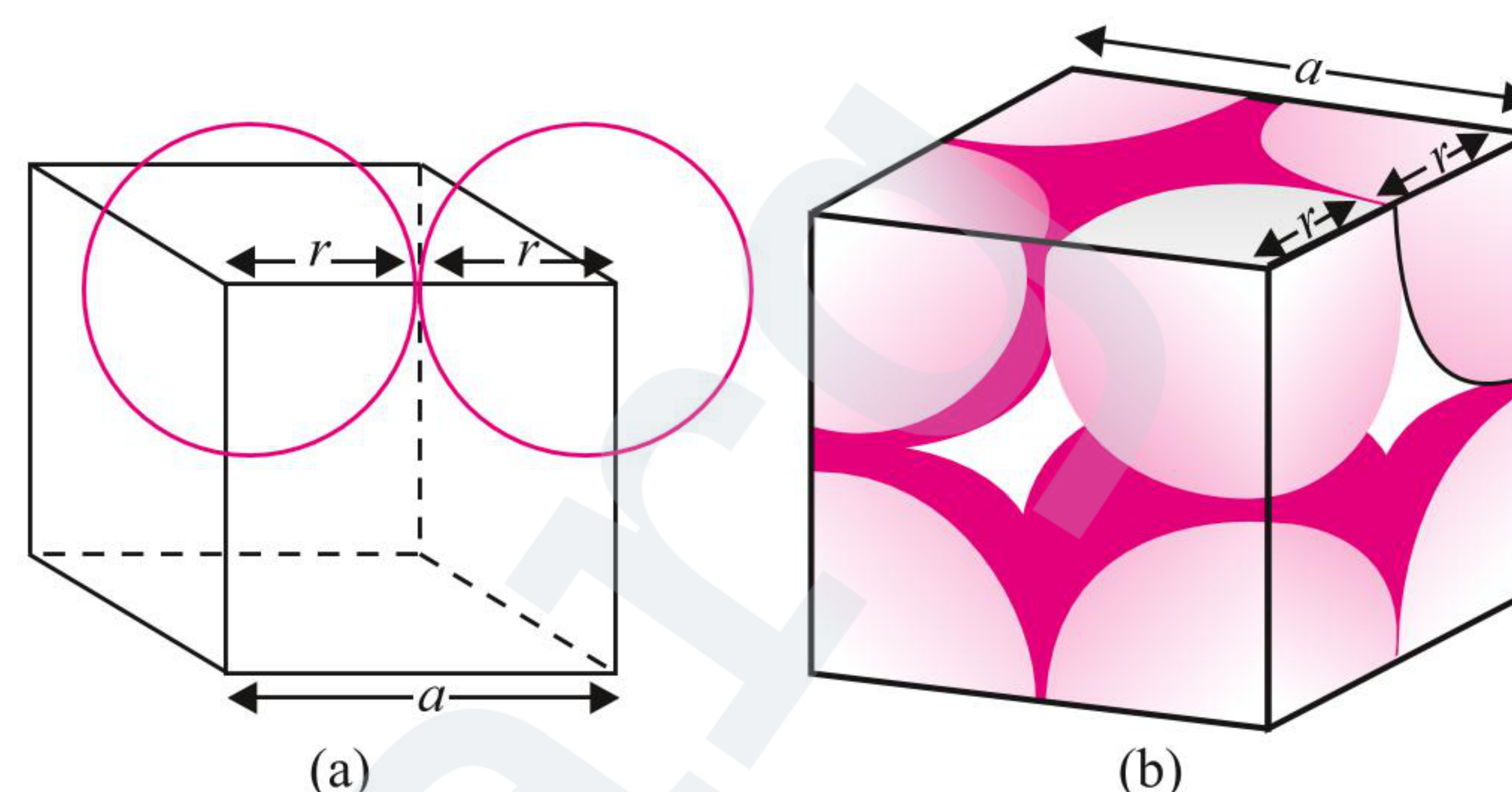


Fig. 1.27 (a) Atomic radius of a simple cube and (b) actual portions of atoms in an sc unit cell

b. Body-centred cubic (bcc)

Each corner of the unit cell touches the body centre atom (not corner atoms) such that

$$2r = \frac{\sqrt{3}}{2}a$$

$$r = \frac{\sqrt{3}}{4}a$$

Alternatively

From Fig. 1.28(a), it is clear that

$$(AC)^2 = (AB)^2 + (BC)^2 = a^2 + a^2 = 2a^2$$

$$(AD)^2 = (AC)^2 + (DC)^2$$

$$(4r)^2 = 2a^2 + a^2$$

$$16r^2 = 3a^2$$

$$\therefore r = \frac{\sqrt{3}}{4}a$$

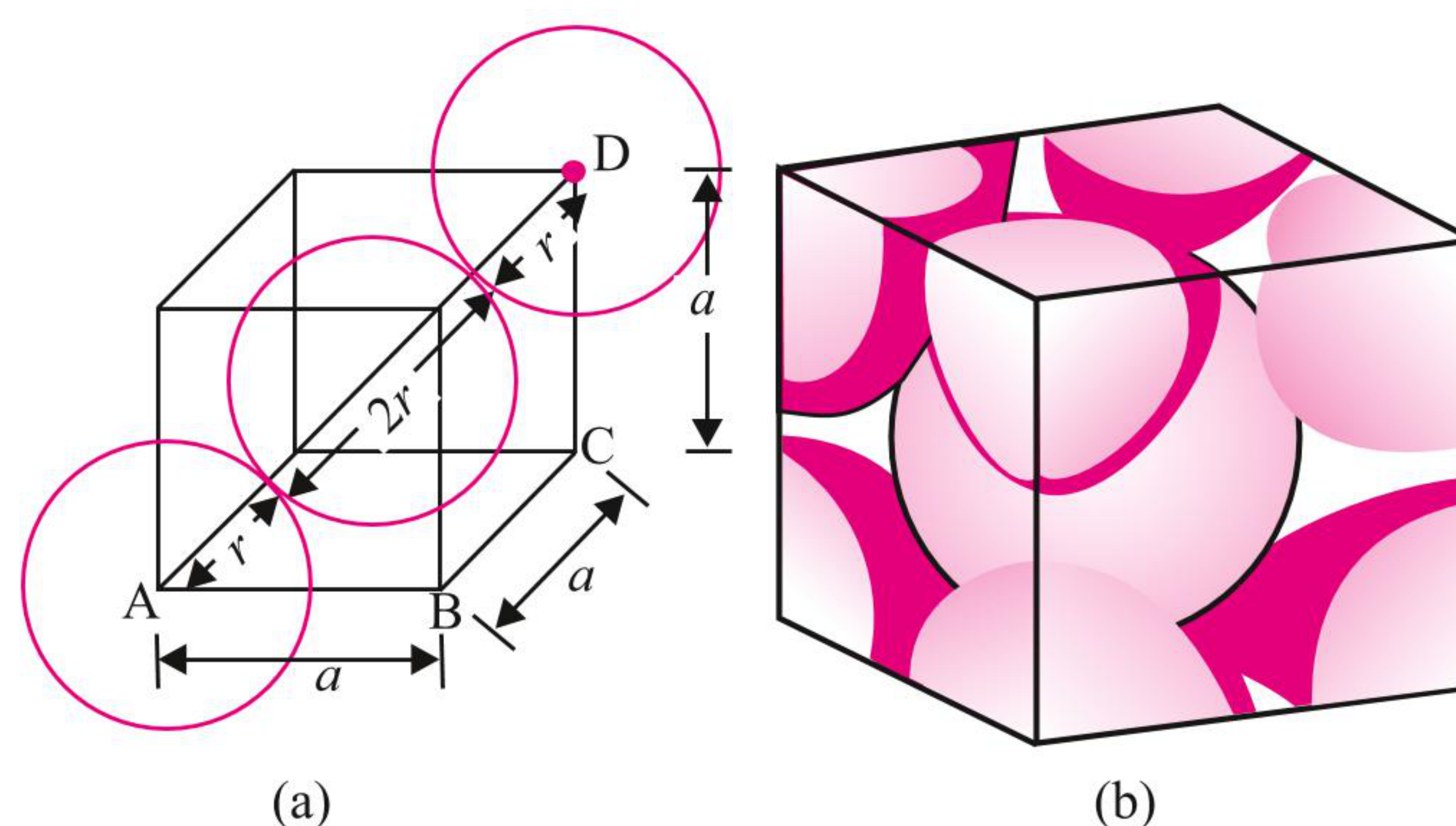


Fig. 1.28 (a) Atomic radius of a bcc and (b) actual portion of atoms in a bcc unit cell

c. Face-centred cubic (fcc)

Each corner of a particular face centre atom touches the other face centre atom (not corner atom) such that

$$2r = \frac{a}{\sqrt{2}} \Rightarrow r = \frac{a}{2\sqrt{2}}$$

Alternatively

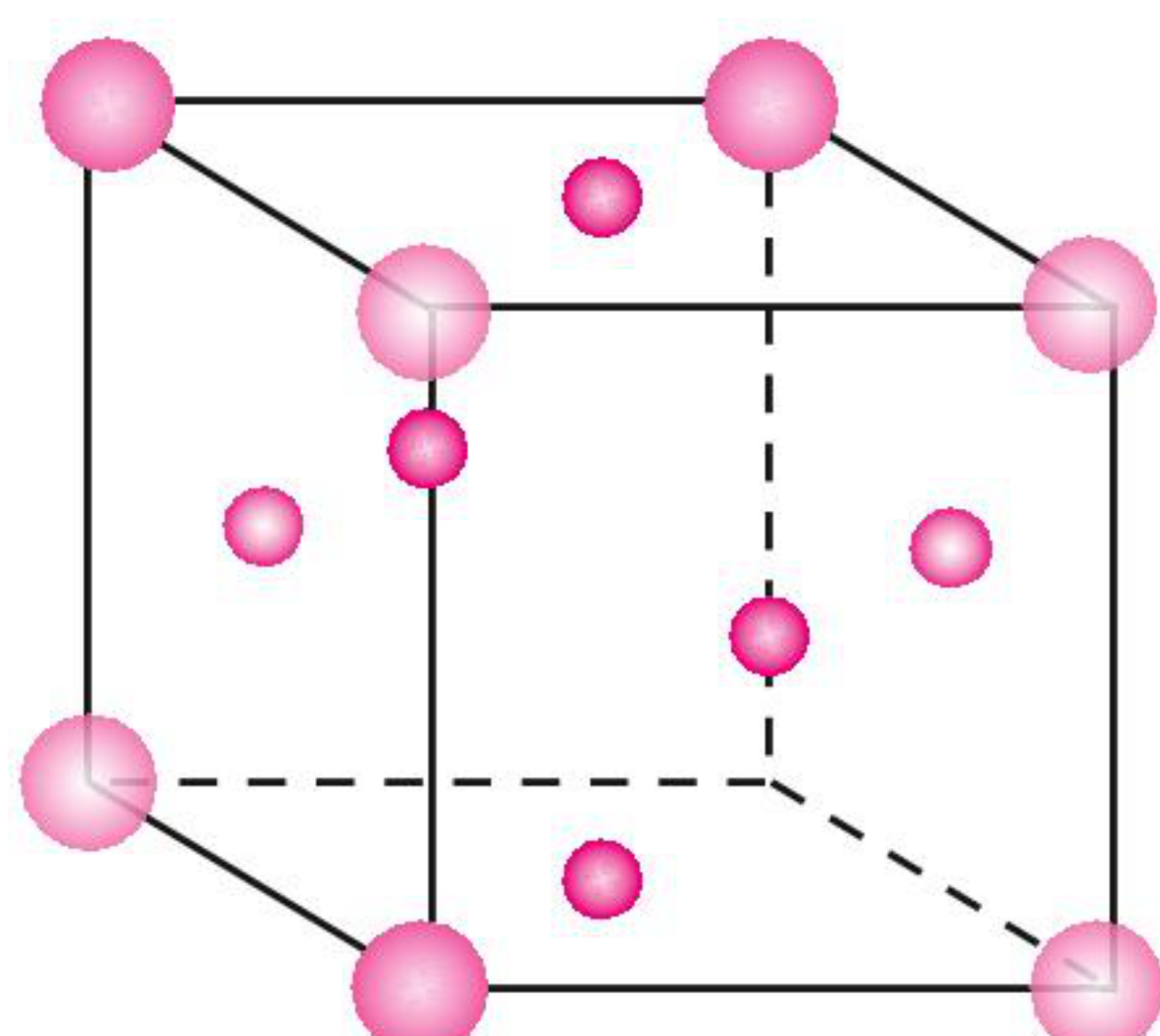
From Fig. 1.29(b), it is clear that

$$(AC)^2 = (AB)^2 + (BC)^2$$

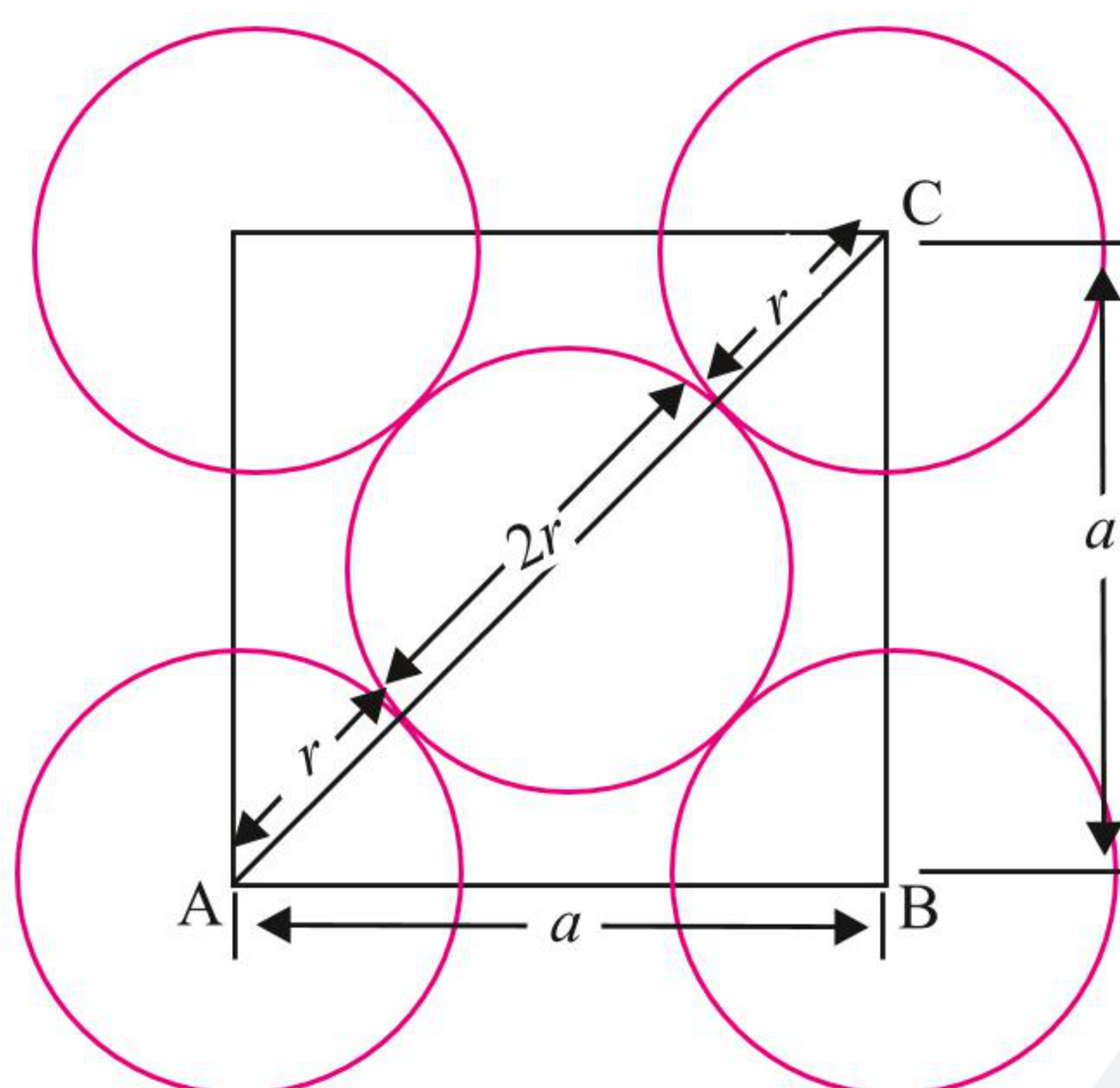
$$(4r)^2 = a^2 + a^2$$

$$\therefore 16r^2 = 2a^2$$

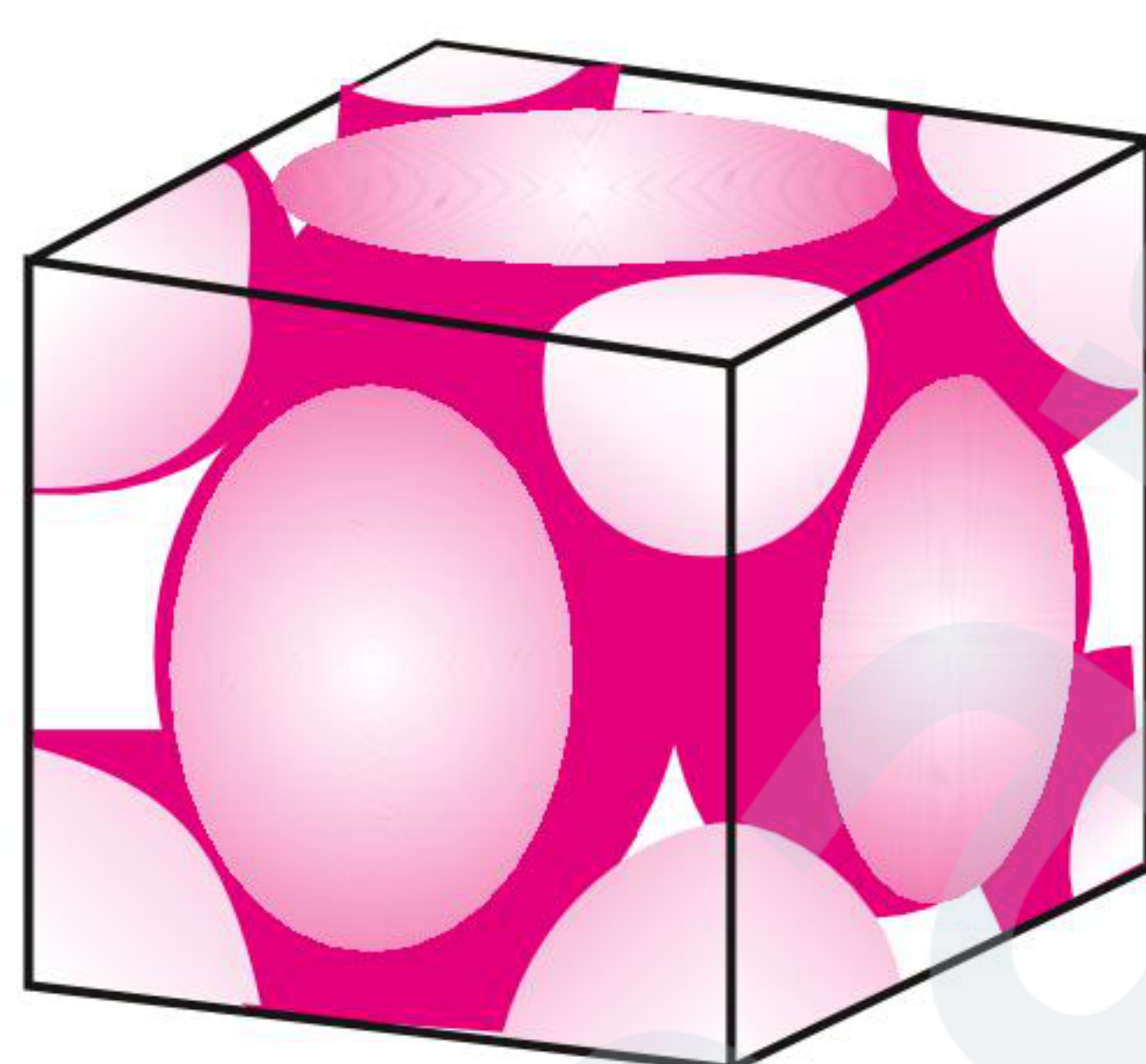
$$\therefore r = \frac{a}{2\sqrt{2}}$$



(a)



(b)



(c)

Fig. 1.29 (a) Unit cell of fcc, (b) view of one face of an fcc unit cell, and (c) actual portion of atoms belonging to the fcc unit cell

Table 1.5 Atomic radius of the atoms in different cubic systems

S.No.	Cubic unit cell	Atomic radius
1.	Simple cubic	$r = a/2$
2.	Body-centred cubic (bcc)	$16r^2 = 3a^2 \Rightarrow r = \frac{\sqrt{3}}{4}a = 0.433a$
3.	Face-centred cubic (fcc)	$16r^2 = 2a^2 \Rightarrow r = \frac{a}{2\sqrt{2}} = 0.3535a$

1.11 COORDINATION NUMBER (CN)

The number of atoms in a crystal which surround a particular atom as its nearest neighbour atoms in its neighbourhood is called its coordination number.

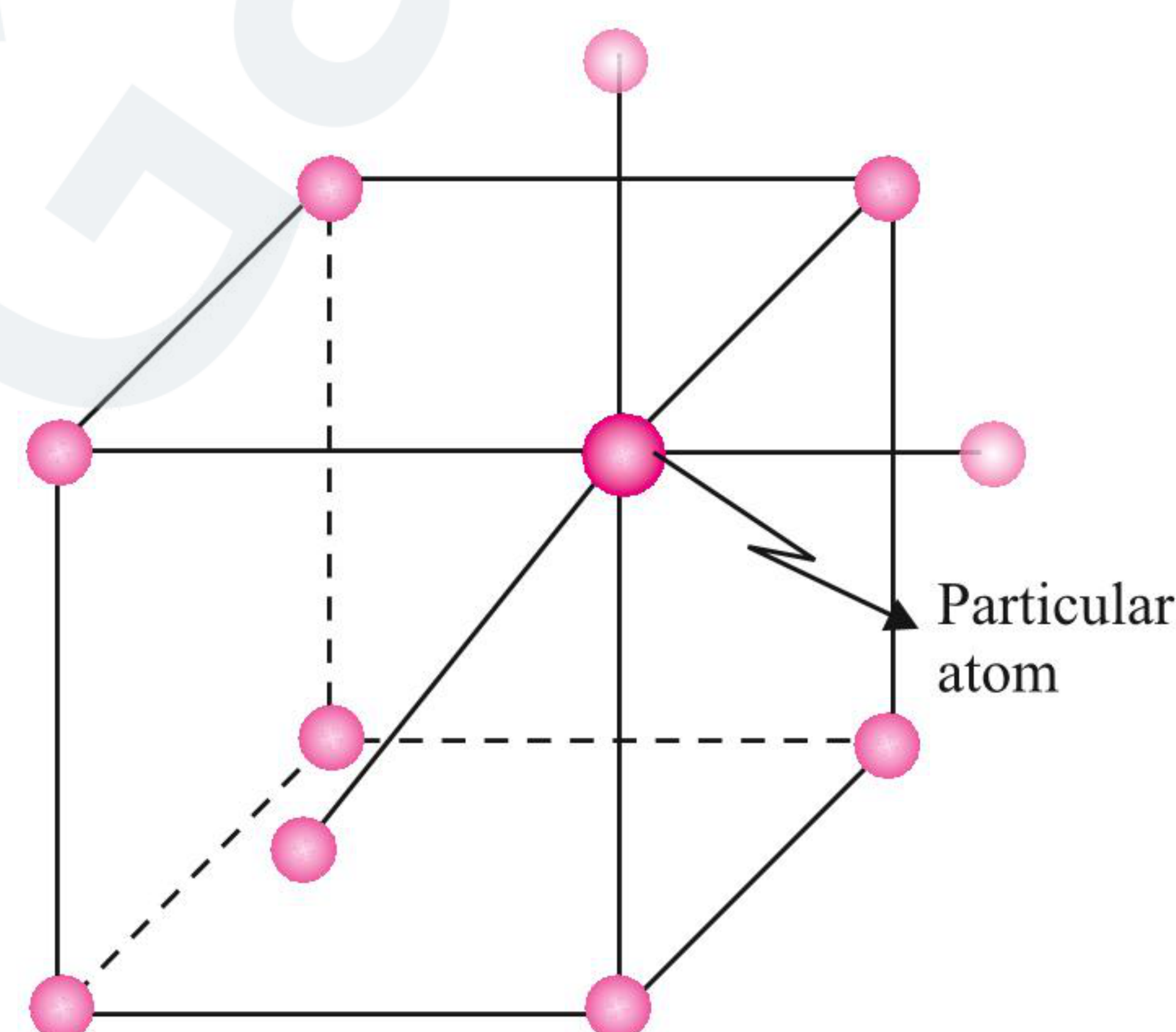
Note:

- For diatomic atoms, coordination number of cations is the number of surrounding anions or vice-versa.
- In crystals with directional bonds, coordination number is lower than that of crystals with non-directional bonds such as metals and ionic compounds.

The coordination number of monoatomic crystals is discussed below.

a. Simple cubic (sc)

Coordination number = 6.



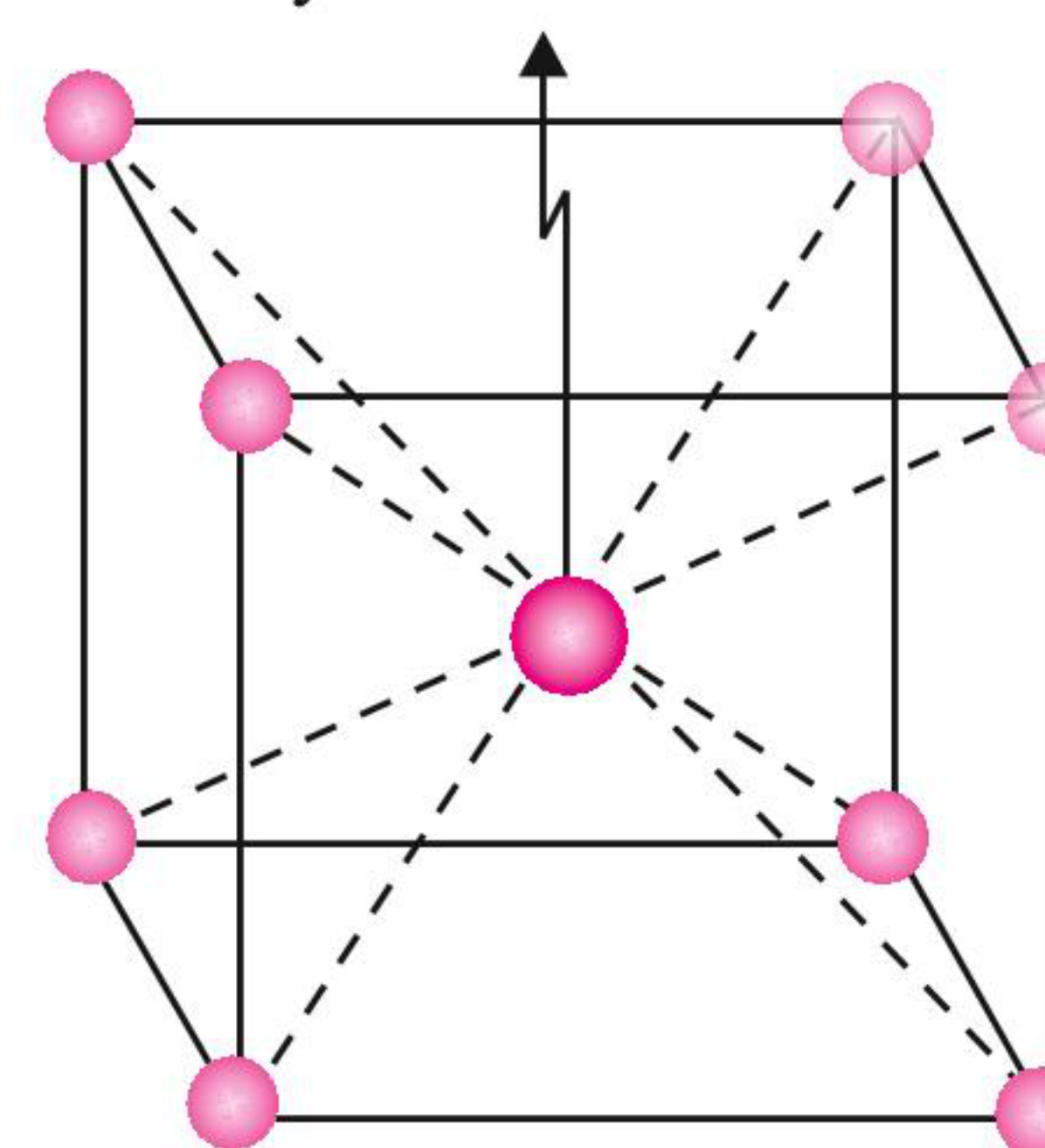
(a)

b. Body-centred cubic (bcc)

Number of atoms surrounding (touching) the body centre atom = 8

Hence, coordination number = 8

Body-centered atom is surrounded by 8 corner atoms



(b)

c. Face-centred cubic (fcc)

Number of atoms surrounding (touching) the face centre of any face = 12

Hence, coordination number = 12

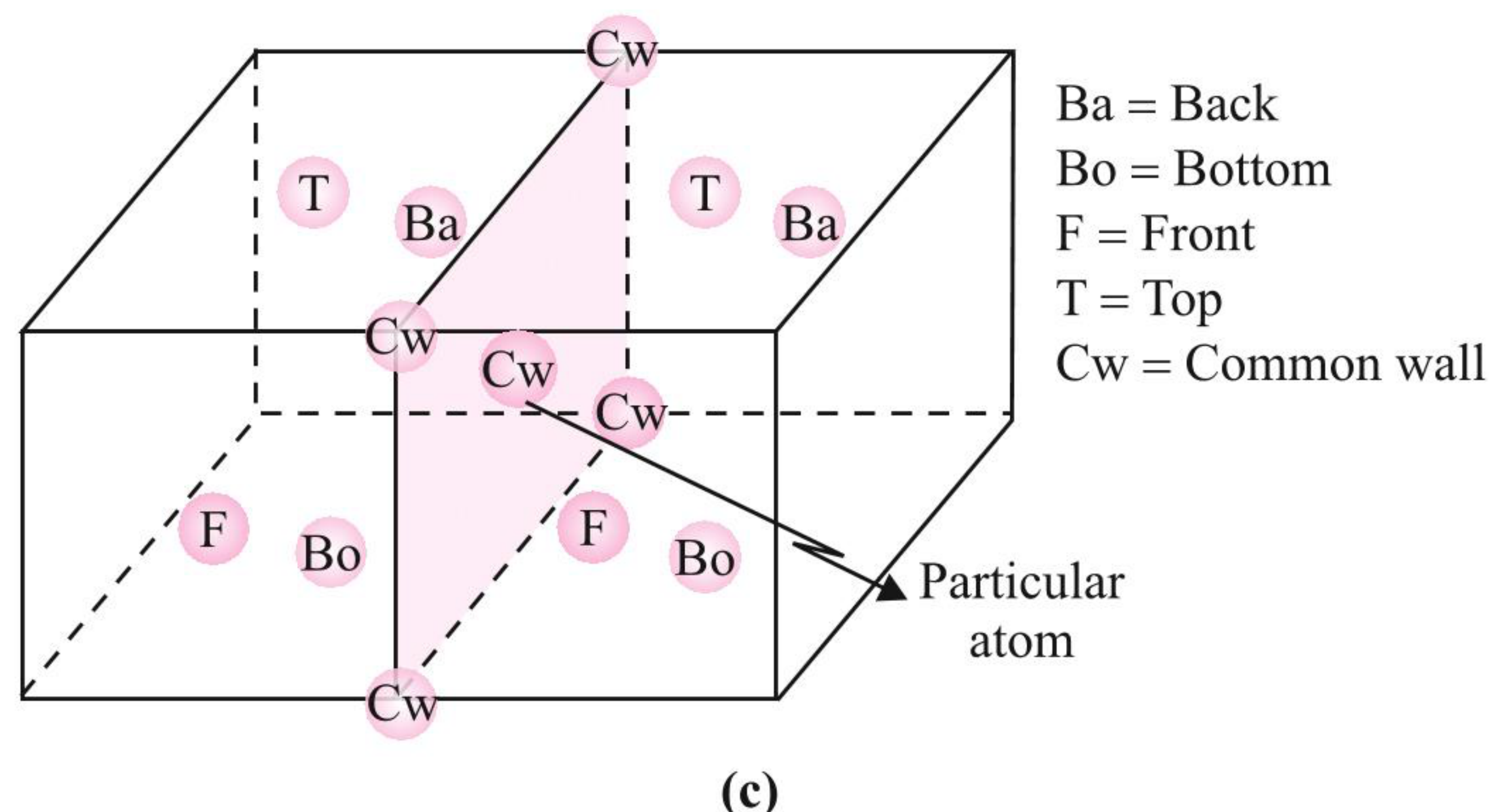


Fig. 1.30 (a) CN in sc (b) CN in bcc (c) CN in fcc

Table 1.6 Coordination number of different cubic systems

S. No.	Cubic unit cell	Coordination number (CN)
1.	Simple cubic (sc)	6
2.	Body-centred cubic (bcc)	8
3.	Face-centred cubic (fcc)	12

1.12 PACKING FRACTION (PF) OR SPACE OCCUPIED BY ATOMS IN A CUBIC SYSTEM

It is the ratio of the volume occupied by the total effective atoms in Z_{eff} in a cubic system to the volume of the unit cell.

$$\begin{aligned}\text{Packing fraction} &= \frac{\text{Volume occupied by effective atoms}}{\text{Volume of the unit cell}} \\ &= \frac{Z_{\text{eff}} \times \text{Volume of atom}}{a^3} \times 100 \\ &= \frac{Z_{\text{eff}} \times \frac{4}{3} \pi r^3}{a^3}\end{aligned}$$

$$\begin{aligned}\text{Packing efficiency} &= \frac{\text{Volume occupied by atoms}}{\text{Volume of unit cell}} \times 100 \\ &= \frac{Z_{\text{eff}} \times \text{Volume of atom}}{a^3} \times 100\end{aligned}$$

a. Simple cube (sc)

Suppose the edge length of a unit cell = a and radius of the sphere = r

$$Z_{\text{eff}} = 1 \text{ atom/unit cell}$$

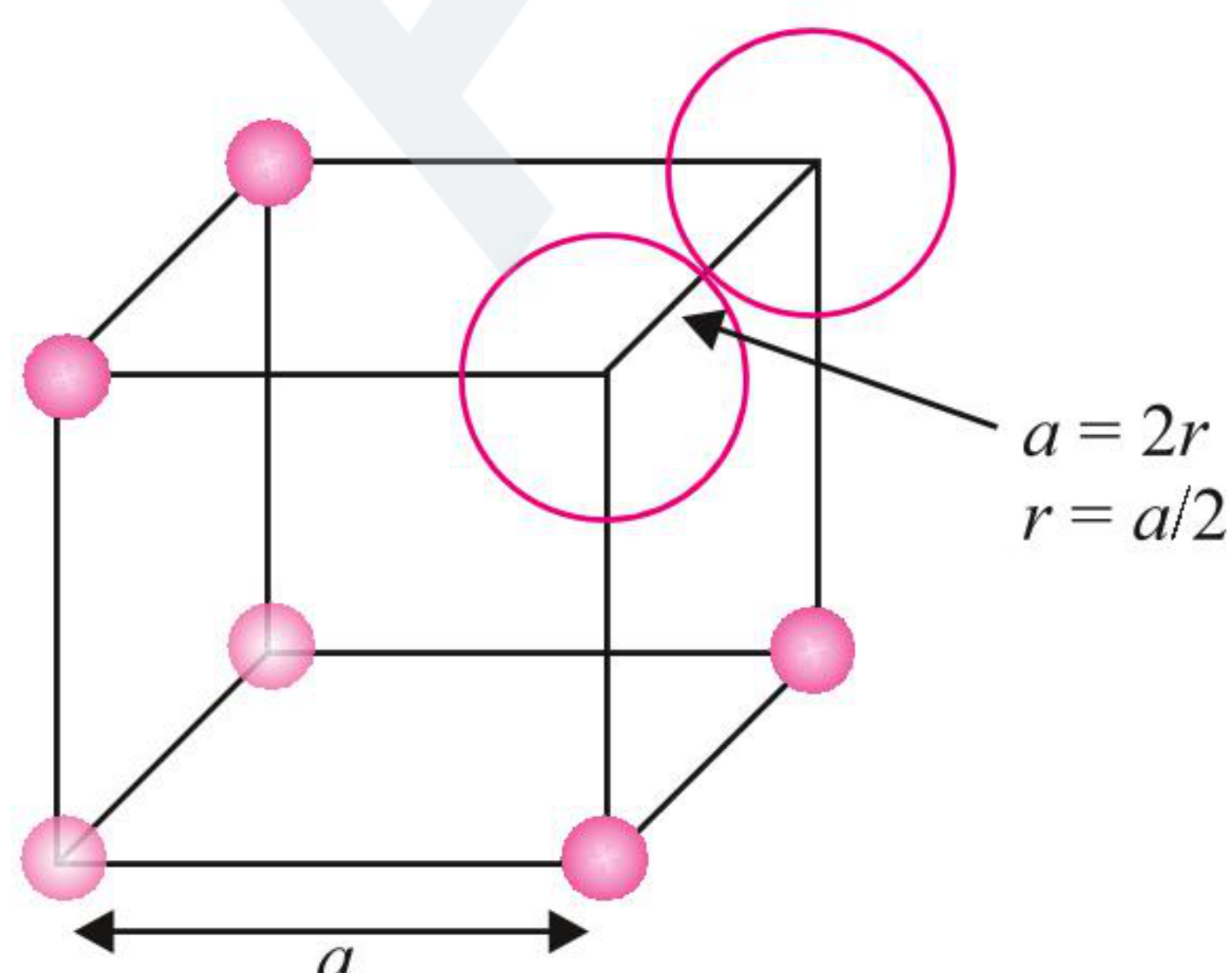


Fig. 1.31 PF in sc

As spheres are touching each other, evidently, $r = \frac{a}{2}$

$$\text{Number of spheres per unit cell} = \frac{1}{8} \times 8 = 1$$

$$\text{Volume of the sphere} = \frac{4}{3} \pi r^3$$

$$\text{Volume of the cube} = a^3$$

$$\text{Packing fraction (PF)} = \frac{Z_{\text{eff}} \times \text{Volume of sphere}}{a^3}$$

$$= \frac{1 \times \frac{4}{3} \pi r^3}{a^3} = \frac{\frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3}$$

$$= \frac{\pi}{6} = 0.524$$

$$\text{Packing efficiency} = \% \text{ space occupied} = 52.4\%$$

$$\begin{aligned}\% \text{ empty space} &= 100 - 52.4 \\ &= 47.6\%\end{aligned}$$

b. Body-centred cubic (bcc)

As the sphere at the centre touches the corner spheres (but corner spheres are not touching each other).

$$Z_{\text{eff}} = 2 \text{ atoms/unit cell}$$

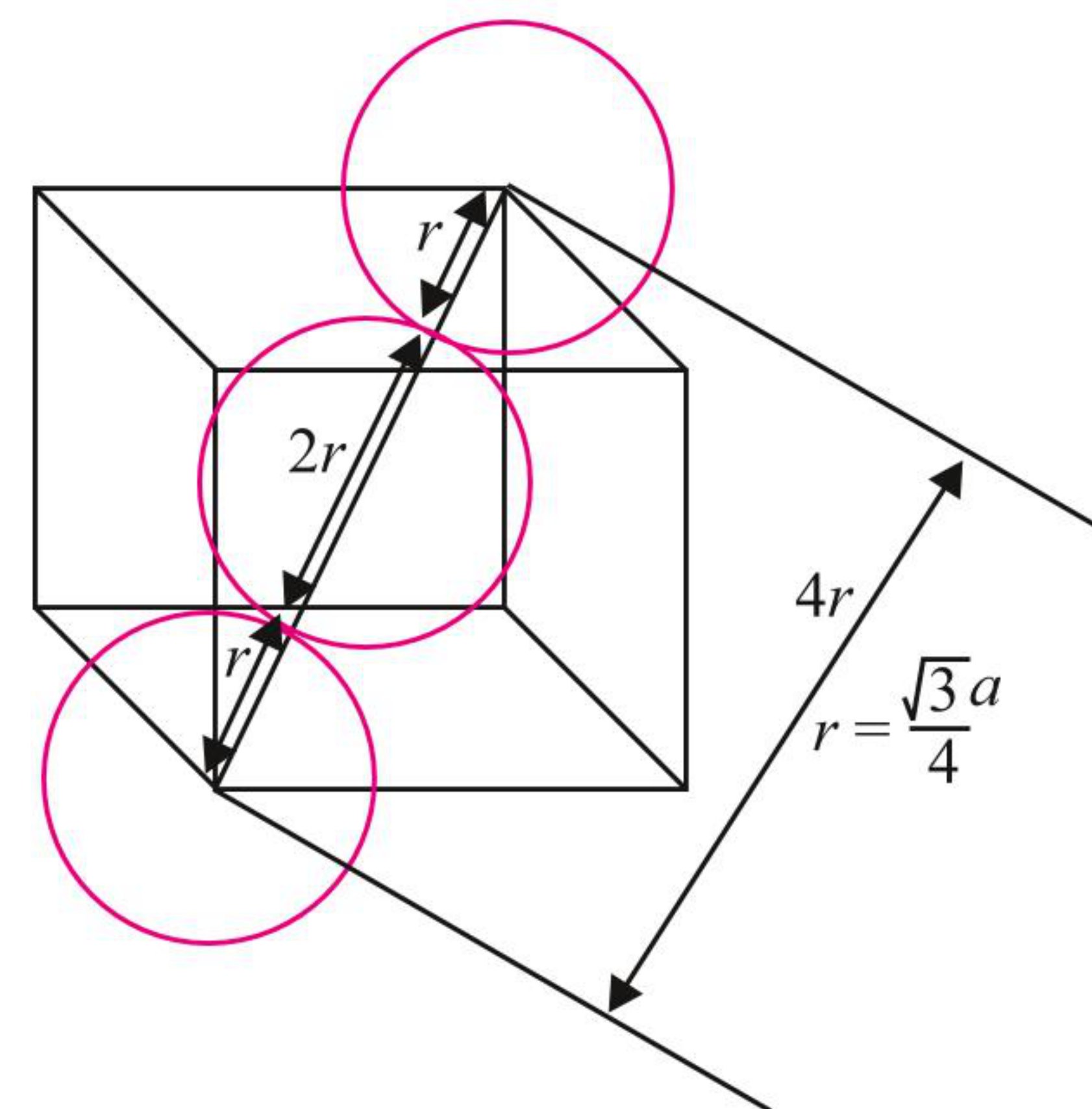


Fig. 1.32 PF in bcc

$$\text{From section 1.10(b), } r = \frac{\sqrt{3}}{4} a$$

$$\text{PF} = \frac{Z_{\text{eff}} \times \frac{4}{3} \pi r^3}{a^3} \quad \dots(i)$$

Substitute the value of r in Eq. (i),

$$\text{PF} = \frac{2 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}}{4} a\right)^3}{a^3} = \frac{\sqrt{3}}{8} \pi = 0.68$$

$$\% \text{ space occupied} = 68\%$$

$$\% \text{ empty space} = 100 - 68 = 32\%$$

c. Face-centred cubic (fcc)

As the spheres on the faces are touching each other (but corner atoms are not touching each other)

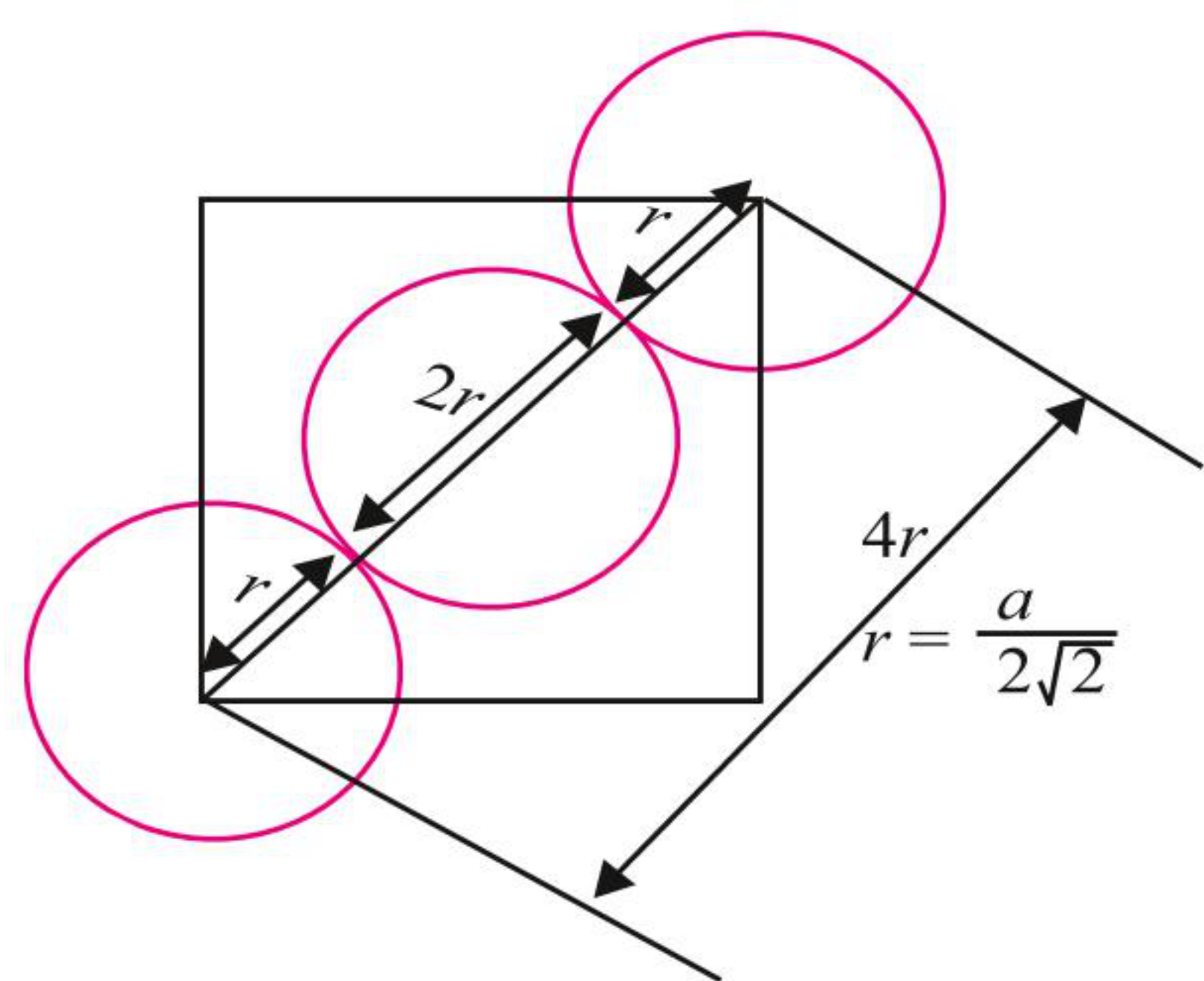


Fig. 1.33 PF in fcc

From section 1.10(c), $r = \frac{a}{2\sqrt{2}}$

$$\text{PF} = \frac{Z_{\text{eff}} \times \frac{4}{3} \pi r^3}{a^3} \quad \dots(i)$$

Substitute the value of r in Eq. (i),

$$\begin{aligned} \text{PF} &= \frac{4 \times \frac{4}{3} \pi \left(\frac{a}{2\sqrt{2}} \right)^3}{a^3} \\ &= \frac{\sqrt{2}}{6} \pi = 0.7404 \end{aligned}$$

% occupied = 74.04%

% empty space $\approx$ 36%

Table 1.7 Packing fraction of different cubic systems

S.No.	Cubic unit cell	Packing fraction (PF)	Packing efficiency (%)
1.	Simple cubic (sc)	$\text{PF} = \frac{\pi}{6} = 0.524$	52.4
2.	Body-centred cubic (bcc)	$\text{PF} = \frac{\sqrt{3}}{8} \pi = 0.68$	68
3.	Face-centred cubic (fcc)	$\text{PF} = \frac{\sqrt{2}}{6} \pi = 0.74$	74

Note:

An fcc unit cell occupies maximum space and hence it is referred as a close packed system.

1.13 CALCULATION OF THE DENSITY OF A METAL BY USING UNIT CELL DIMENSIONS

From the unit cell dimensions, the volume of a unit cell can be calculated. Similarly, from the density of a metal, the mass of the atoms in a unit cell can be calculated. The determination of the mass of a single atom provides an accurate method of determination of Avogadro's constant.

Let a be the edge length of a unit cell of a cubic crystal determined by X-ray diffraction method, ρ be the density of the solid substance, and Mw be the molar mass.

Thus, for a cubic crystal

$$\begin{aligned} \text{Volume of unit cell} &= a^3 \\ &= (a \text{ pm})^3 \\ &= (a \times 10^{-10} \text{ cm})^3 \\ &= a \times 10^{-30} \text{ cm}^3 \end{aligned}$$

Note:

$$1 \text{ pm} = 10^{-12} \text{ m} = 10^{-10} \text{ cm}.$$

$$\begin{aligned} \text{Mass of unit cell} &= \text{Number of atoms in unit cell } (Z_{\text{eff}}) \\ &\quad \times \text{Mass of each atom } (m) \\ &= Z_{\text{eff}} \times m \end{aligned}$$

Mass of an atom present in the unit cell is given by:

$$m = \frac{Mw}{N_A} \quad \left(\begin{array}{l} Mw = \text{Molar mass} \\ N_A = \text{Avogadro's constant} \end{array} \right)$$

Therefore, the density of the unit cell is:

$$\begin{aligned} \rho &= \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}} \\ &= \frac{Z_{\text{eff}} \times m}{a^3 \times 10^{-30}} = \frac{Z_{\text{eff}} \times Mw}{a^3 \times N_A \times 10^{-30}} \text{ g cm}^{-3} \end{aligned}$$

If Mw is in g mol^{-1} , then a^3 must be taken in cm^3 .

In terms of SI units, Mw is given in kg mol^{-1} , then a^3 must be taken in m^3 .

$$\text{Then, } \rho = \frac{Z_{\text{eff}} \times Mw}{N_A \times a^3} \text{ kg m}^{-3}$$

The density of the substance is same as the density of the unit cell. The above equation involves five parameters. Knowing any four, the fifth can be calculated.

Table 1.8 Densities of cubic systems

S. No.	Cubic unit cell	Z_{eff}	Density (ρ) (g cm^{-3})
1.	Simple cubic (sc)	1	$\rho = \frac{1 \times Mw}{N_A \times a^3 \times 10^{-30}}$
2.	Body-centred cubic (bcc)	2	$\rho = \frac{2 \times Mw}{N_A \times a^3 \times 10^{-30}}$
3.	Face-centred cubic (fcc)	4	$\rho = \frac{4 \times Mw}{N_A \times a^3 \times 10^{-30}}$

Alternatively (for monoatomic crystal)

Density is defined as the ratio of mass of unit cell and volume of unit cell.

$$\begin{aligned} \rho &= \frac{\text{Mass of atoms present in unit cell}}{\text{Volume of unit cell}} \\ &= \frac{(Z_{\text{eff}}) \times (Mw \text{ in amu})}{6.023 \times 10^{23} \times a^3} \left[\frac{1}{6.023 \times 10^{23}} = 1.67 \times 10^{-24} \right] \\ &= \frac{(Z_{\text{eff}} \times Mw \text{ in amu}) \times 1.67 \times 10^{-24} \text{ g}}{a^3} \\ &= \frac{(Z_{\text{eff}} \times Mw \text{ in amu}) \times 1.67 \times 10^{-27} \text{ kg}}{a^3} \end{aligned}$$

In general,

$$\rho = \frac{\Sigma (\text{Number of atoms of each kind}) \times (M_w \text{ of each kind in amu}) \times 1.67 \times 10^{-27} \text{ kg}}{a^3}$$

$$\text{(Number of formula units)} \\ \text{or } \rho = \frac{\times (M_w \text{ of the compound}) \times 1.67 \times 10^{-27} \text{ kg}}{a^3}$$

Table 1.9 Summary of various characteristics of different cubic systems

S. No.	Cubic unit cell	Number of effective atoms per unit cell (Z_{eff})	Coordination number (CN)	Atomic radius (r)	Packing efficiency	Density (ρ) (g cm^{-3})	Nearest neighbour distance (d)
1.	Simple cube (sc)	1	6	$r = \frac{a}{2}$	$\text{PE} = \frac{\pi}{6} \times 100 = 52.36\%$	$\rho = \frac{Z_{\text{eff}} \times M_w}{N_A \times a^3 \times 10^{-30}} = \frac{1 \times M_w}{N_A \times a^3 \times 10^{-30}}$	a
2.	Body-centred cubic (bcc)	2	8	$r = \frac{\sqrt{3}}{4} a$	$\text{PE} = \frac{\sqrt{3}}{8} \pi \times 100 = 68 \%$	$\rho = \frac{2 \times M_w}{N_A \times a^3 \times 10^{-30}}$	$\frac{\sqrt{3}}{2} a$
3.	Face-centred cubic (fcc)	4	12	$r = \frac{a}{2\sqrt{2}}$	$\text{PE} = \frac{\sqrt{2}}{6} \pi \times 100 = 74.04\%$	$\rho = \frac{4 \times M_w}{N_A \times a^3 \times 10^{-30}}$	$\frac{a}{\sqrt{2}}$

ILLUSTRATION 1.9

Consider the parallelograms shown in the figure (i) representing two-dimensional unit cells.

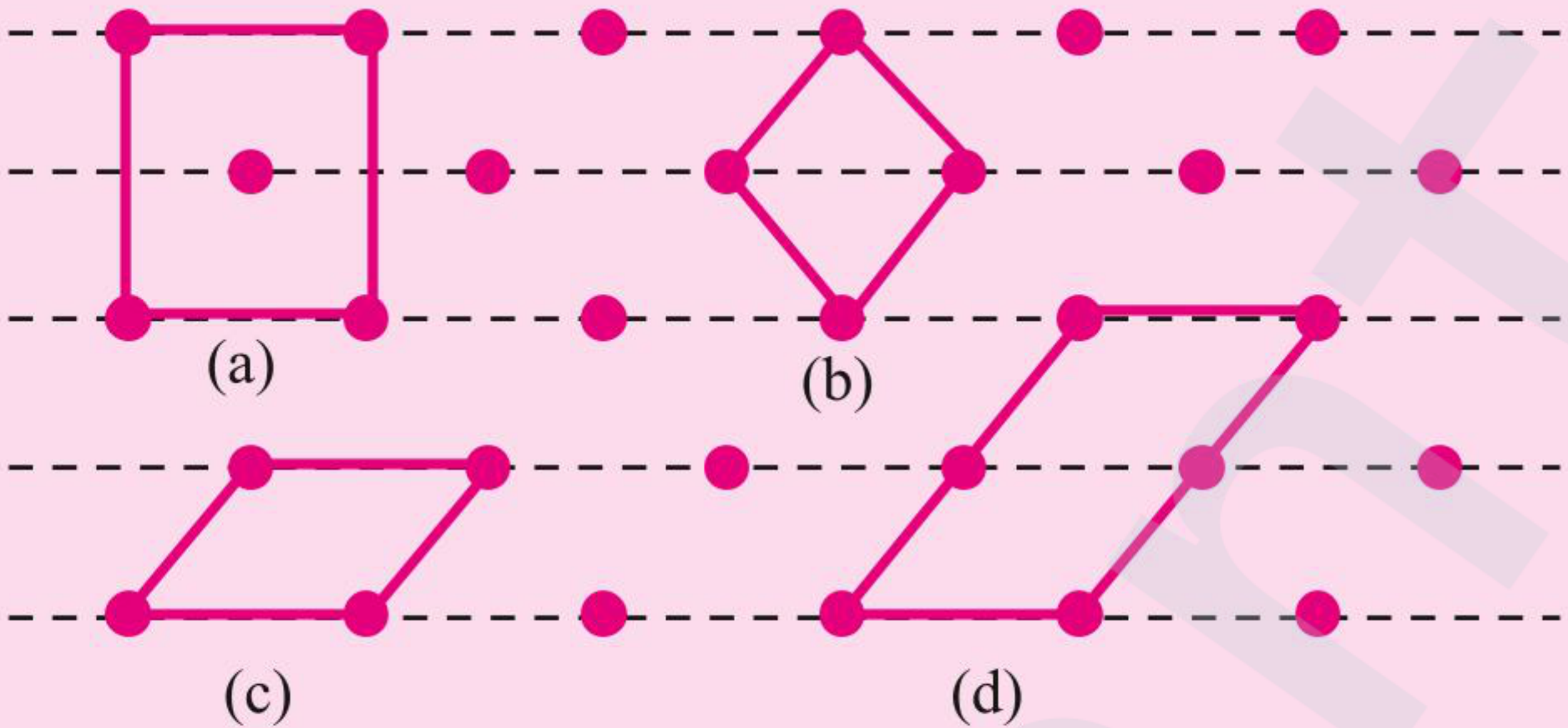


Fig. (i)

- What is the content of the unit cell as shown in figure (i)?
- In Fig. (i) which of these are primitive and which are multiple unit cells? Are any of these orthogonal?
- How many nearest neighbour circles does a given circle have in the figure (ii)?
- What is the relation between the radius of circle and the length of parallelogram for the unit cell shown in the figure below (space filling diagram)?

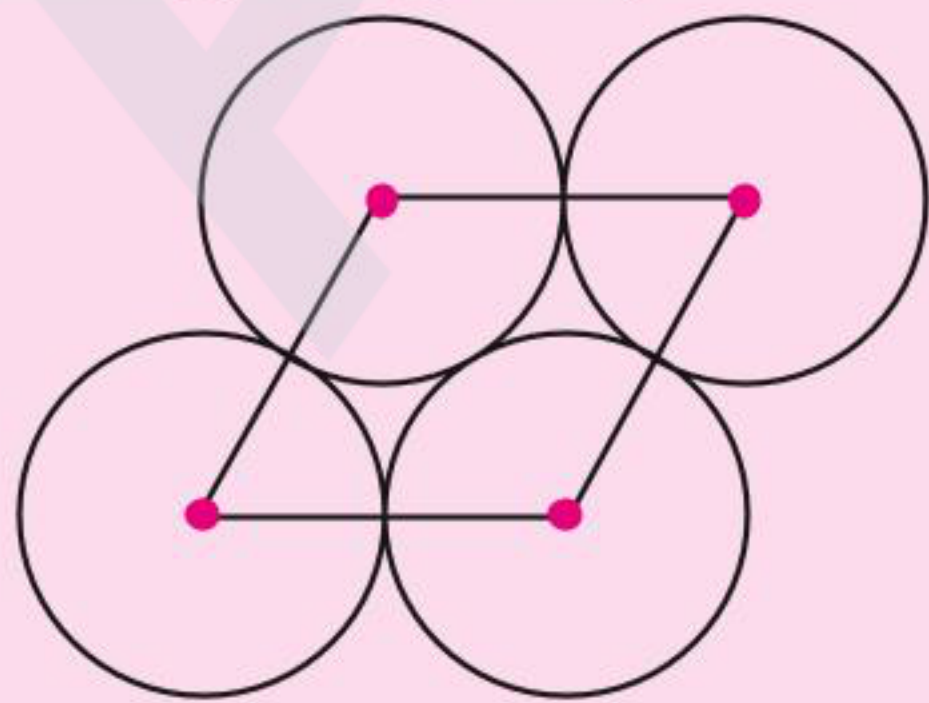


Fig. (ii)

- What is the packing fraction of the unit cell in the figure (ii)?
- What is the radius of the triangular hole shown in the figure (ii)?

Sol.

- The unit cell content (Z) is the total number of atoms contained within the unit cell. From the (b) in Fig. (ii), only part of each circle at each corner is contained within the parallelogram unit cell.

Note: Remember it is a 2D unit cell.

Each circle is touching 4 other circles, so share of each circle is $\frac{1}{4} \Rightarrow Z = \frac{1}{4} \times 4 = 1$.

- Primitive unit cells are (b) and (c), because the only points contained in the unit cell are at the corners of the parallelograms. Unit cell (a) and (d) are multiple unit cells because there are points in the unit cells in addition to the corners of the parallelogram. Unit cell (a) is an orthogonal unit cell because it contains angles of 90° .
- The crystal coordination number (CN) is the number of nearest neighbours around a given atom, ion, or molecule in the crystal. From the first figure (i), each atom (except the “surface” atom) is touching 6 other atoms, so $\text{CN} = 6$.
- $a = 2R$, where a is the length of the side of parallelogram and R is the radius of circle.
- Packing fraction = $\frac{\text{Area occupied by circles}}{\text{Area of unit cell}}$

Since $Z = 1$, area of circle = πR^2

$$\text{Area of parallelogram} = 2\sqrt{3}R^2$$

$$\therefore \text{PF} = \frac{Z \times \pi R^2}{2\sqrt{3}R^2} = \frac{\pi}{2\sqrt{3}} = 0.907$$

f. (Refer section 1.15.2).

Let R is the radius of larger circle and r is the radius of the triangular hole:

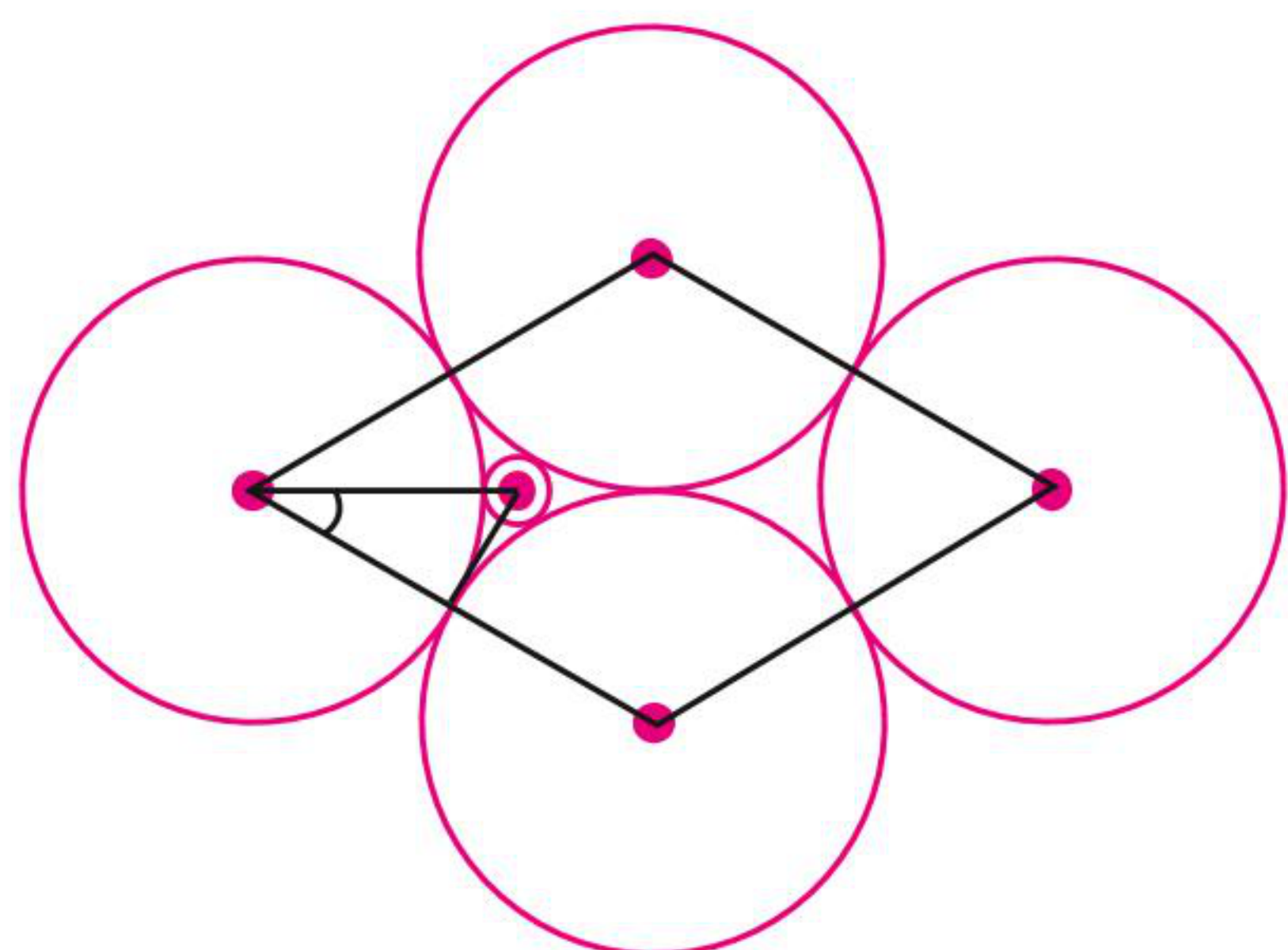


Fig. (iii)

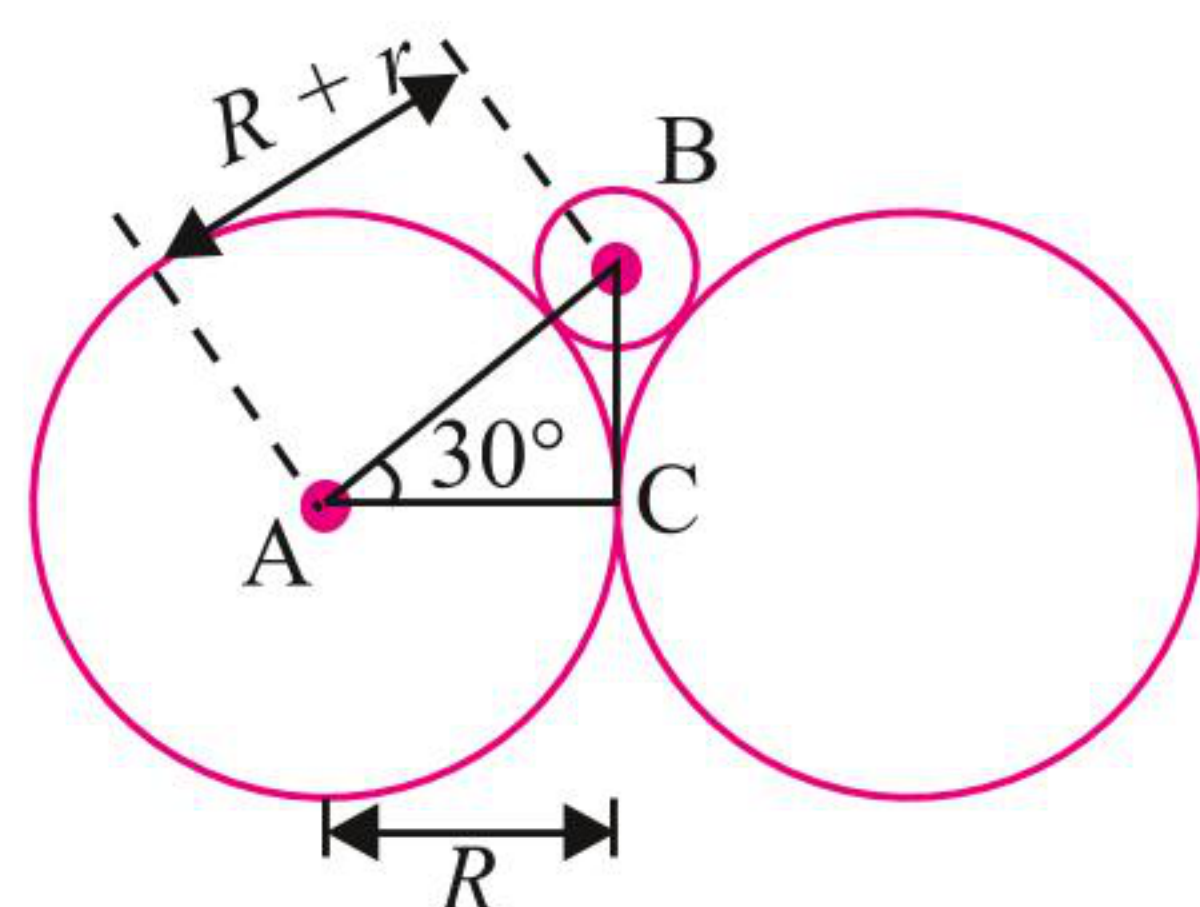


Fig. (iv)

$$\begin{aligned} \text{In } \triangle ABC, \cos 30^\circ &= \frac{\text{Base}}{\text{Hypotenuse}} = \frac{AC}{AB} = \frac{R}{R+r}, \\ \Rightarrow (R+r) \cos 30^\circ &= R, \\ \Rightarrow r &= \left(\frac{2}{\sqrt{3}} - 1 \right) R \end{aligned}$$

ILLUSTRATION 1.10

Why uncharged atoms or molecules never crystallize in simple cubic structures?

Sol. Uncharged atoms and molecules pack more effectively in close-packed structures. Thus they never crystallise in simple cubic structures.

ILLUSTRATION 1.11

Why an end-centred unit cell cannot be cubic? What is the minimum possible symmetry for this type of unit cell?

Sol. A cubic unit cell must have all the six faces the same. But for end centered unit cell, $a \neq b \neq c$. Thus minimum symmetry possible for an end centred unit cell is orthorhombic or monoclinic..

ILLUSTRATION 1.12

Why a hexagonal close-packed structure and a cubic close-packed structure for a given element would be expected to have the same density?

Sol. The two structures have the same coordination number, hence the same packing efficiency.

1.14 CLOSE-PACKED STRUCTURES

In order to understand the packing of the constituent particles in a crystal, it is assumed that the constituent particles are identical hard spheres. The constituent particles in solids are close packed in such a way that they occupy maximum available space leaving minimum vacant space, and hence the crystal has maximum density. The building of these identical hard spheres in a three-dimensional structure occurs in three steps:

a. Close packing in one dimension

There is only one way of arranging spheres in a one-dimensional close-packed structure, that is, to arrange them in a row touching each other (Fig. 1.34).

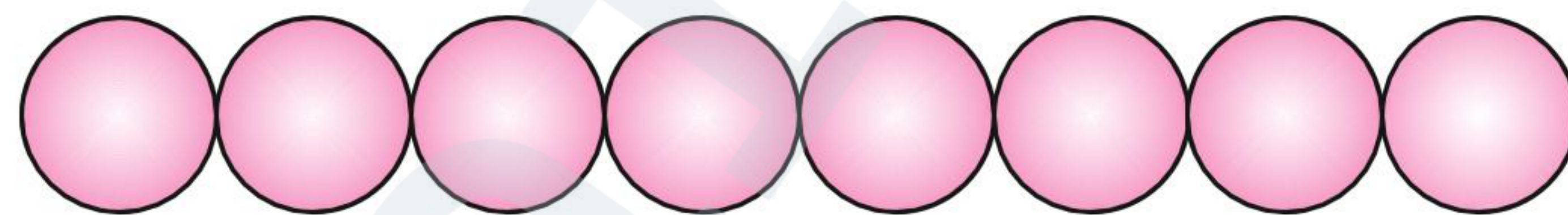


Fig. 1.34 Close packing of spheres in one dimension

In this arrangement, each sphere is in contact with two of its neighbours. The number of nearest neighbours of a particle is called its coordination number. Thus, in one-dimensional close-packed arrangement, the coordinate number is 2.

b. Close packing in two dimensions

A two-dimensional close-packed structure can be constructed by stacking (placing) the rows of close-packed spheres. This can be done in two different ways.

i. The second row may be placed in contact with the first one such that the spheres of the second row are exactly above those of the first row. The spheres of the two rows are aligned horizontally as well as vertically. If we call the first row as "A" type row, the second row being exactly the same as the first one, is also of "A" type. Similarly, we may place more rows to obtain AAA type of arrangement as shown in Fig. 1.35 (a).

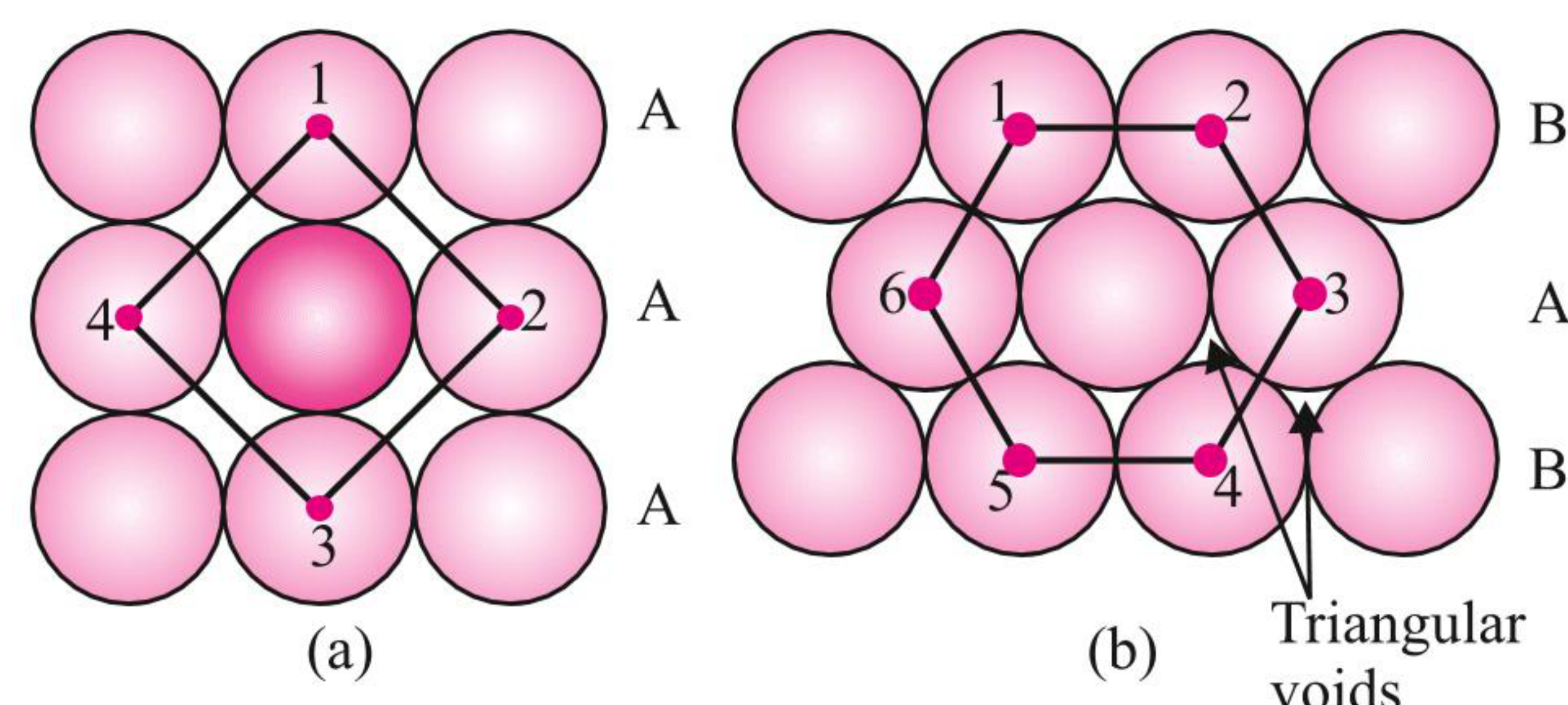


Fig. 1.35 (a) Square close packing and (b) hexagonal close packing in two dimensions

In this arrangement, each sphere is in contact with four of its neighbours. Thus, the two-dimensional coordination number is 4. Also, if the centres of these four immediate neighbouring spheres are joined, a square is formed. Hence, this packing is called *square close packing in two dimensions*. But this type of packing is not efficient as more vacant space is left by the spheres in this arrangement.

ii. The second row may be placed above the first one in a staggered manner such that its spheres fit in the depressions of the first two. If the arrangement of

spheres in the first row is called “A” type, the one in the second row is different and may be called “B” type. When the third row is placed adjacent to the second in a staggered manner, its spheres are aligned with those of the first layer. Hence, this layer is also of “A” type. The spheres of similarly placed fourth row will be aligned with those of the second row (“B” type). Hence, this arrangement is of ABAB type. In this arrangement, there is less free space and this packing is more efficient than the square close packing. Each sphere is in contact with six of its neighbours and the two-dimensional coordination number is 6. The centres of these six spheres are at the corners of a regular hexagon [Fig. 1.35(b)]. Hence this packing is called *two-dimensional hexagonal close packing*. It can be seen in Fig. 1.35(b) that in this layer there are some voids (empty spaces). These are triangular in shape. The triangular voids are of two different types. In one row, the apex of the triangles are pointing upwards and in the next layer downwards [Fig. 1.35(b)].

c. Close packing in three dimensions

All real structures are three-dimensional structures. They can be obtained by placing two-dimensional layers one above the other. Types of three-dimensional close packing are as below.

- i. **Three-dimensional close packing from two-dimensional square close-packed layers:** The second layer is placed over the first layer such that the spheres of the upper layer are exactly above those of the first layer. In this arrangement, spheres of both the layers are perfectly aligned horizontally as well as vertically as shown in (Fig. 1.36). Similarly, place more layers one above the other. If the arrangement of spheres in the first layer is called “A” type, all the layers have the same arrangement. Thus, this lattice has AAA... type pattern. The lattice thus formed is the simple cubic lattice, and its unit cell is the primitive cubic unit cell (Fig. 1.23).

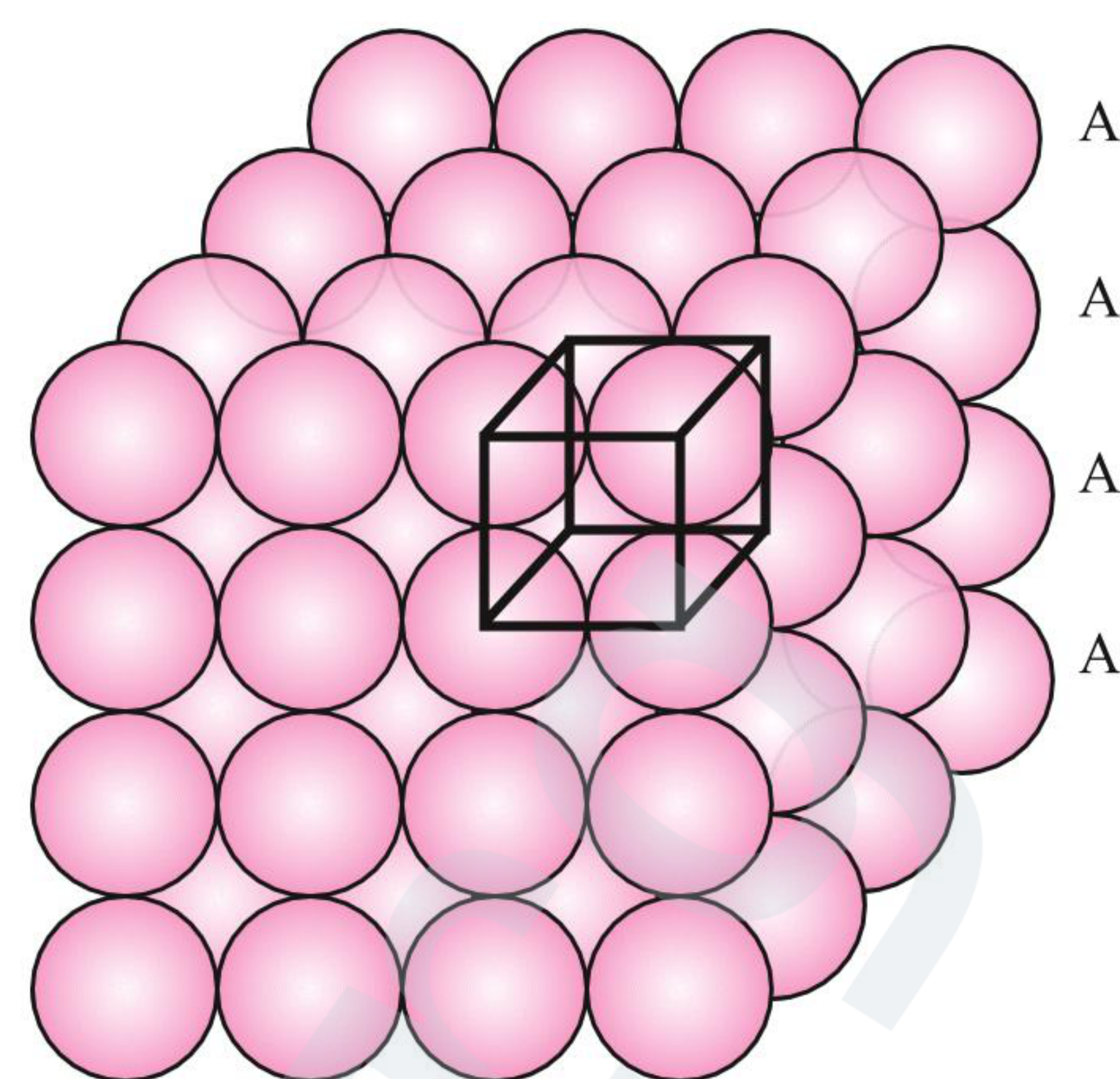


Fig. 1.36 Simple cubic lattice formed by AAA... arrangement

- ii. **Three-dimensional close packing from two-dimensional hexagonal close layers:** A three-dimensional close-packed structure can be formed by packing layers one over the other.

1. **Placing the second layer over the first layer:** Take a two-dimensional hexagonal close-packed layer “A” and place a similar layer above it such that the spheres of the second layer are placed in the depressions of the first layer since the spheres of the two layers are aligned differently. It can be observed from Fig. 1.37 that not all the triangular voids of the first layer are covered by the spheres of the second layer. This gives rise to different arrangements. Wherever a sphere of the second layer is above the void of the first layer (or vice versa) a tetrahedral void is formed. These voids are called *tetrahedral voids* because a tetrahedron is formed when the centres of these four spheres are joined. They have been marked as “T” in Fig. 1.37. One such void has been shown separately in Fig. 1.38.

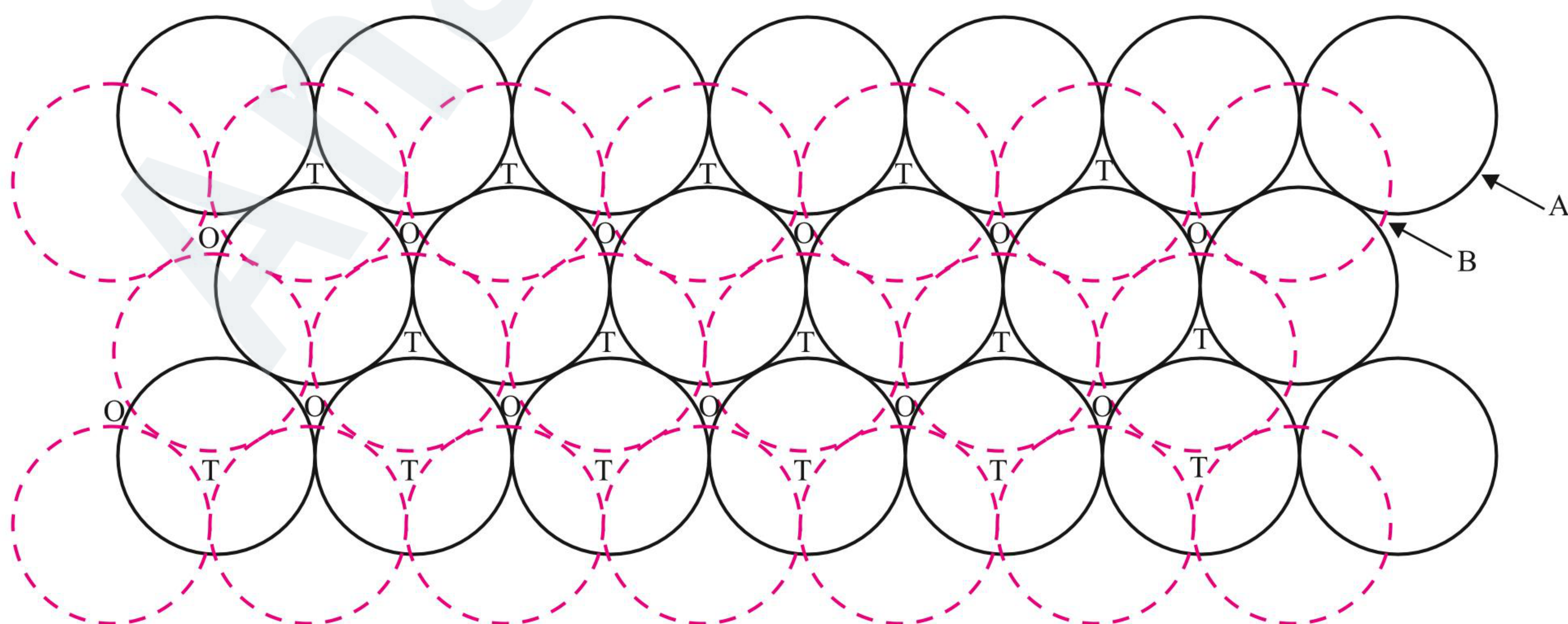


Fig. 1.37 A stack of two layers of close-packed spheres and voids generated in them. T = Tetrahedral void; O = Octahedral void

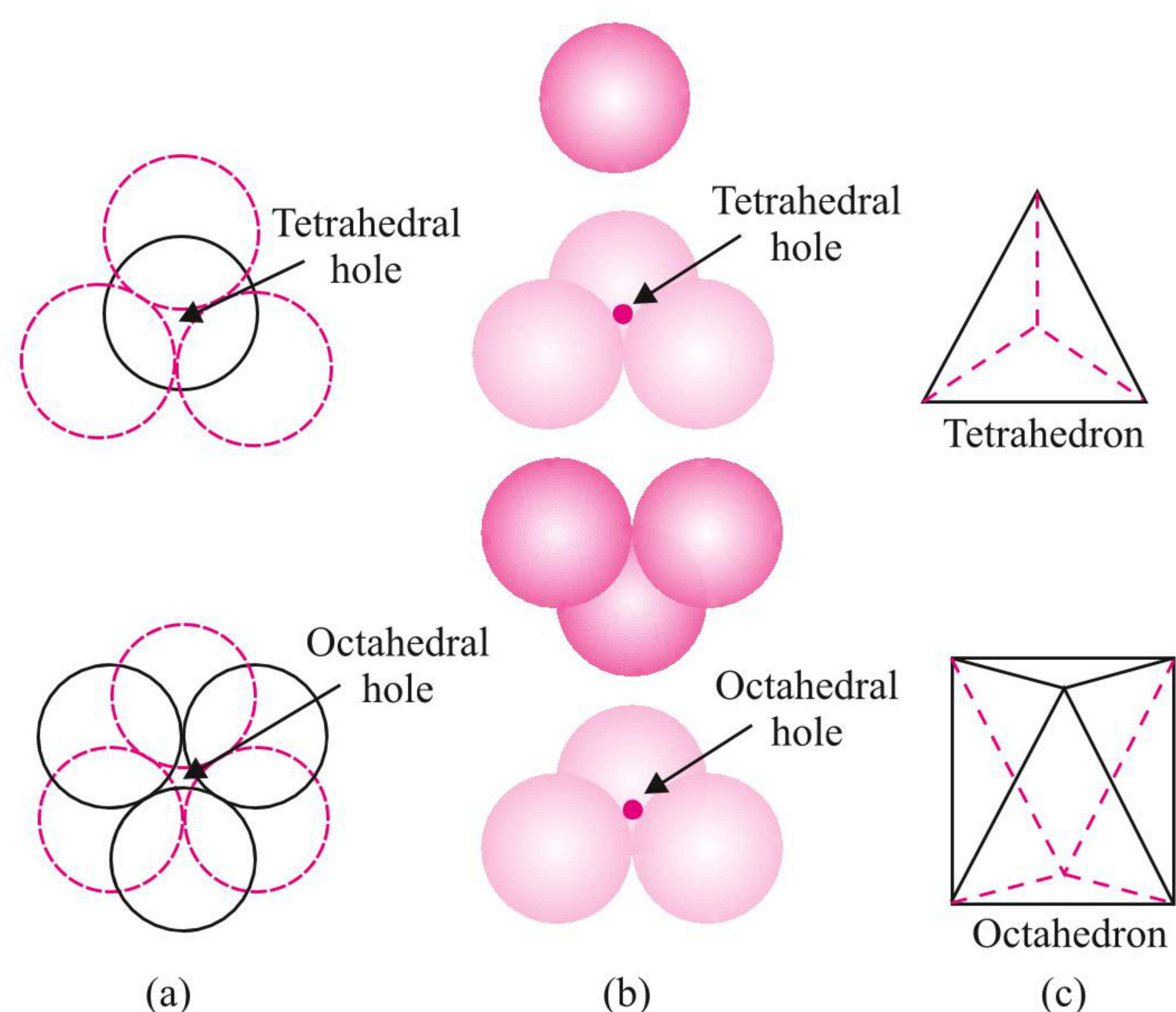


Fig. 1.38 Tetrahedral and octahedral voids: (a) top view, (b) exploded side view, and (c) geometrical shape of the void

At other places, the triangular voids in the second layer are above the triangular voids in the first layer, and the triangular shapes of these do not overlap. One of them has the apex of the triangle pointing upwards and the other downwards. These voids have been marked as “O” in Fig. 1.37. Such voids are surrounded by six spheres and are called *octahedral voids*. One such void has been shown separately in Fig. 1.38. The number of these two types of voids depend upon the number of close-packed spheres.

Let the number of close-packed spheres be N , then:

The number of octahedral voids formed = N

The number of tetrahedral voids formed = $2N$

2. *Placing the third layer over the second layer:*

When third layer is placed over the second, there are two possibilities.

- *Covering tetrahedral voids:* Tetrahedral voids of the second layer may be covered by the spheres of the third layer. In this case, the spheres of the third layer are exactly aligned with those of the first layer. Thus, the pattern of spheres is repeated in alternate layers. This pattern is often written as ABAB... pattern. This structure is called hexagonal close-packed (hcp) structure (Figs. 1.39 and 1.40). This type of arrangement of atoms is found in many metals such as magnesium and zinc.

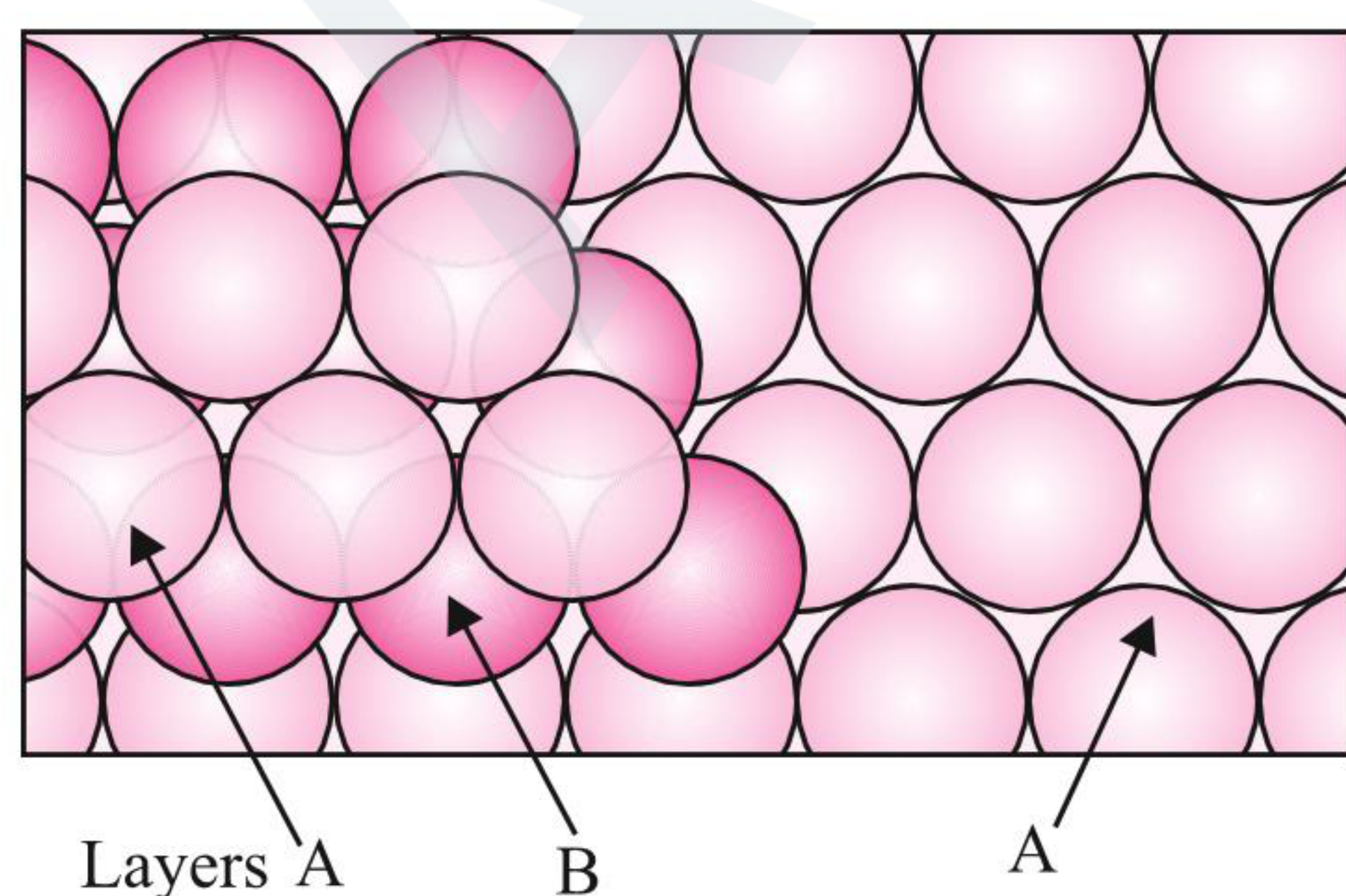


Fig. 1.39 The third layer of spheres lies above the spheres of the first layer to give an AB AB AB... structure (hcp packing)

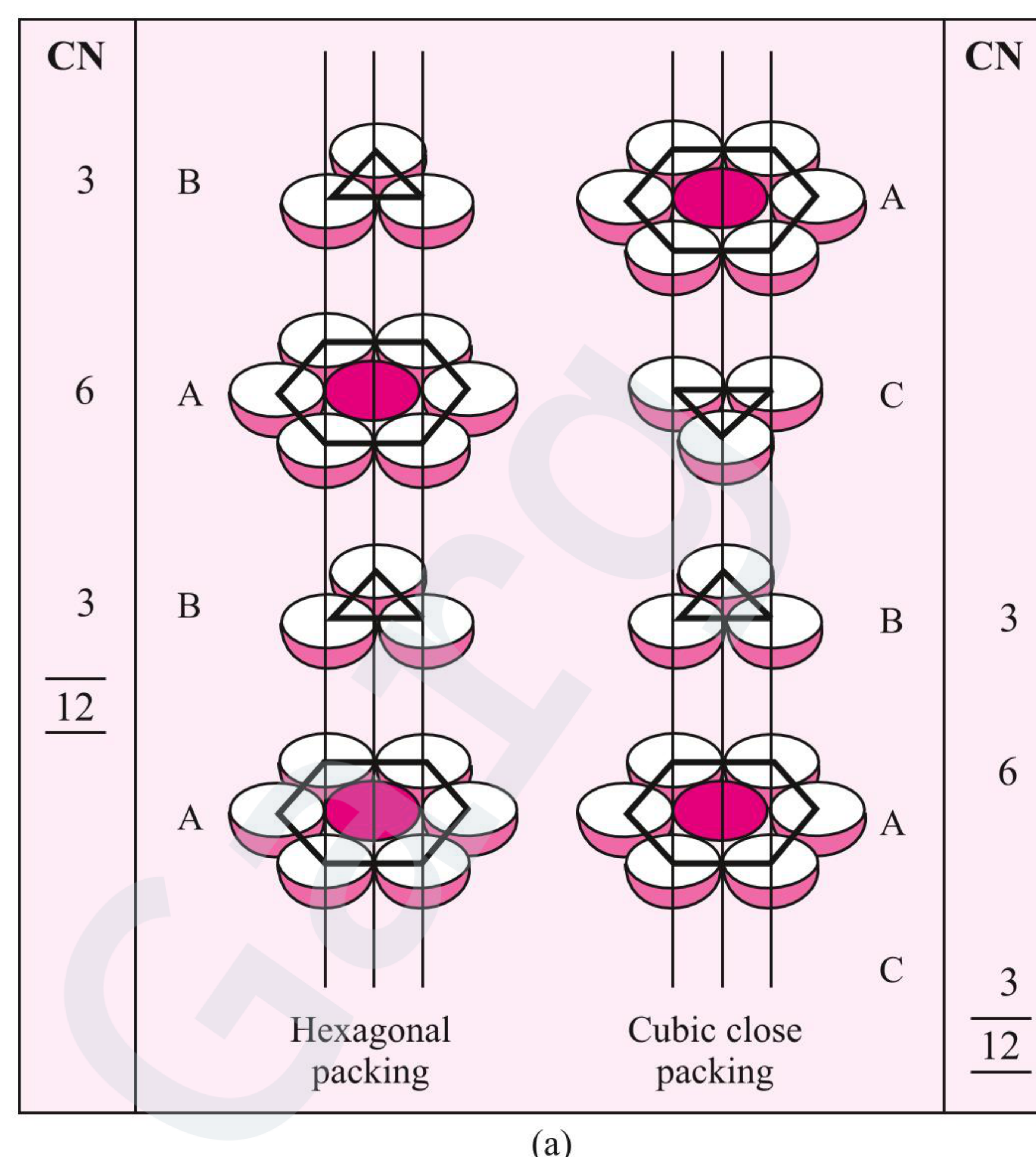


Fig. 1.40 (a) Hexagonal and cubic close packing exploded view showing stacking of layers of spheres, (b) four layers stacked in each case, and (c) geometry of packing

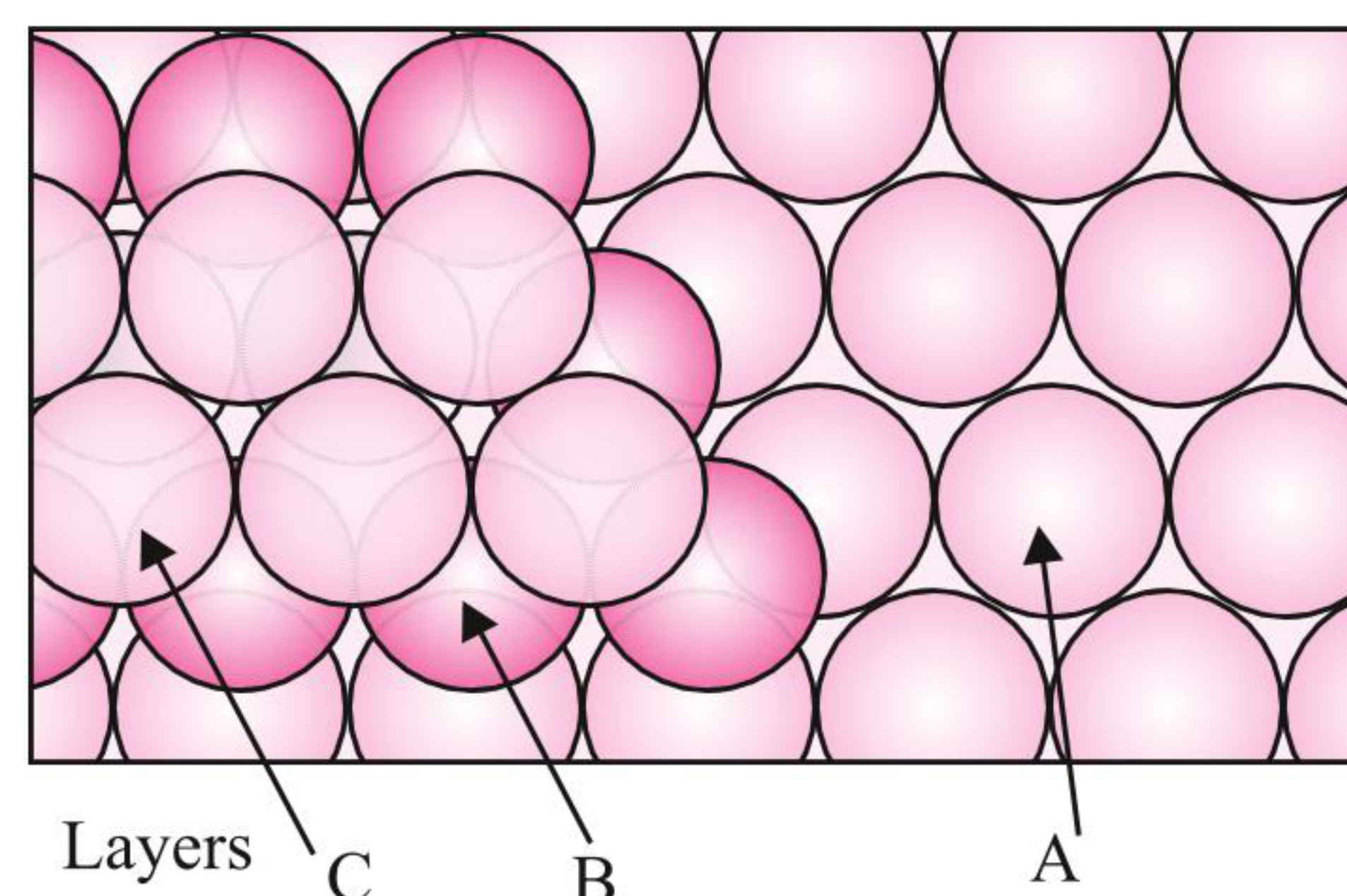


Fig. 1.41 The spheres of the third layer can lie above the depressions in the first layer to give an ABC ABC... arrangement of layers (ccp packing)

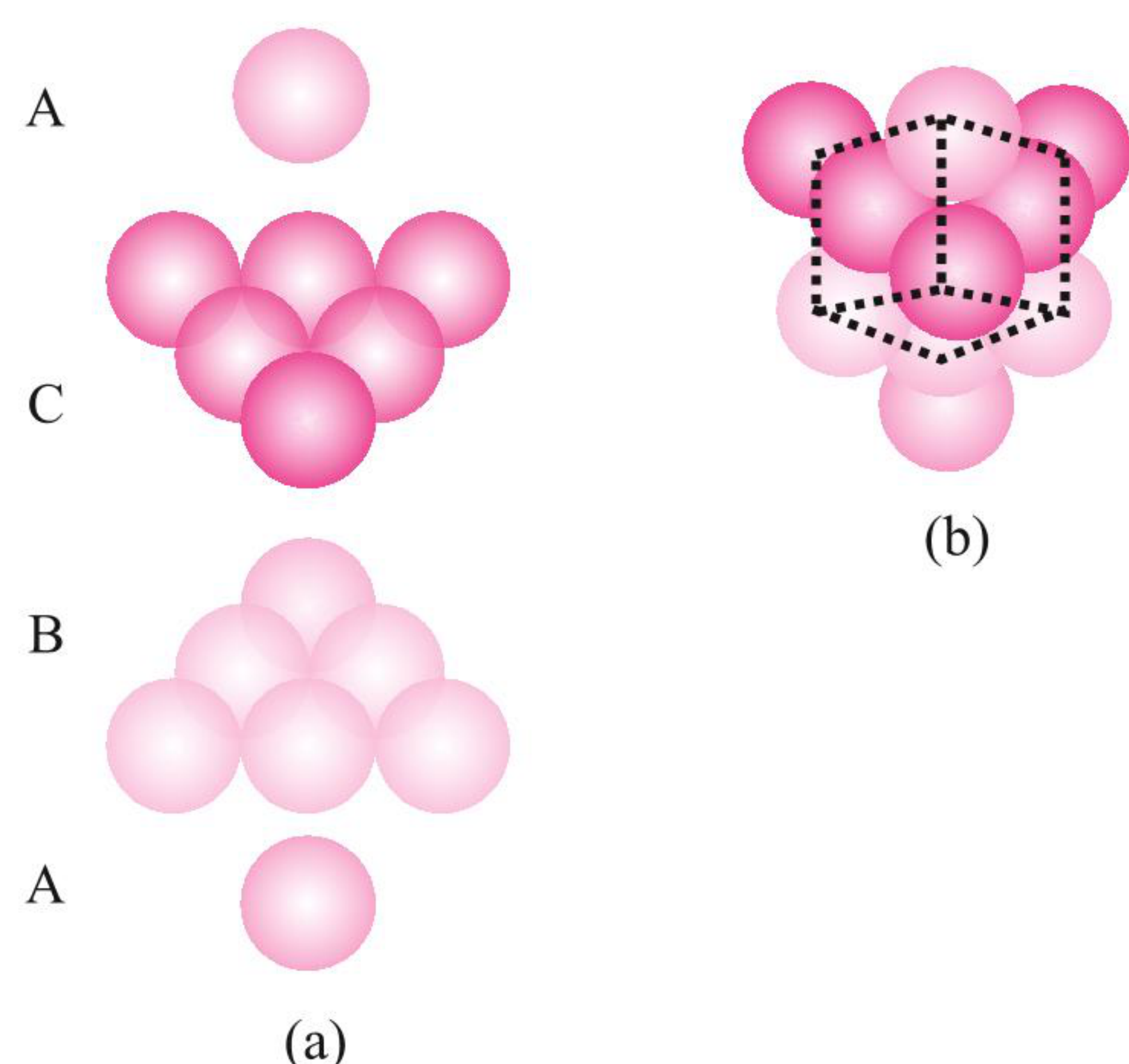


Fig. 1.42 (a) An ABC ABC... arrangement of layers when octahedral void is covered; (b) a fragment of structure formed by this arrangement resulting in a cubic close-packed (ccp) or face-centred cubic (fcc) structure

- **Covering octahedral voids:** The third layer may be placed above the second layer in a manner such that its spheres cover the octahedral voids. When placed in this manner, the spheres of the third layer are not aligned with those of either the first or the second layer. This arrangement is called “C” type. Only when the fourth layer is placed, its spheres are aligned with those of the first layer as shown in Figs. 1.40 to 1.42. This pattern of layers is often written as ABC ABC ... This structure is called cubic close-packed structure (ccp) or face-centred cubic (fcc) structure. Metals such as copper, silver, and gold crystallize in the structure.

1.14.1 COORDINATE NUMBER (CN) OF HCP AND CCP STRUCTURES

- a. CN of an hcp structure:** In an hcp structure, each sphere has three nearest neighbours in the plane below (B), six in its own plane (A), and three in the one above (B), having 12 spheres in all at equal distances. Alternatively, this means that the number of nearest neighbours called *coordination number* of each atom in this arrangement of solid is 12 [Fig. 1.43(a)]. It is impossible to pack identical spheres together with a coordination number greater than 12. The close-packed structure adopted by a metal is associated with lowest energy.

In crystals with directional bonds, the coordination number is lower compared to crystals with non-directional bonds (as in the case of metals and ionic compounds).

- b. CN of a ccp structure:** In a ccp structure, each sphere has three nearest neighbours in the plane below (C), six in its own plane (A), and three in the plane above (B), having 12 spheres in all at equal distances. So CN of ccp structure is also 12 [Fig. 1.43(b)].

So hcp, ccp, or fcc are close-packed structures occupying maximum space (74%) while 26% space remaining vacant. In contrast to this, packing in bcc structure is not that efficient and only 68% is occupied by the atoms.

The voids or holds in crystals are also called *interstices*. Their size acquire importance in relation to the formation of transition metal hydrides, borides, carbides, and nitrides

in which the respective non-metals (H, B, C, and N) are accommodated in the interstices. That is why these compounds are called *interstitial compounds*.

CN	(a) hcp	(b) ccp	CN
	A	C	
3	B	B	3
6	A	A	6
3	B	C	3
12			12

Fig. 1.43 A simplified view of (a) hexagonal closed packing (AB AB ... pattern) and (b) cubic close packing (ABC ABC ... pattern)

Table 1.10 Crystal lattices and coordination numbers of the various types of metallic crystals

Metallic elements	Lattice type	Coordination no.
Be, Mg, Cd, Zn, Ti	Hexagonal close packing (hcp)	12
Cu, Ca, Sr, Ag, Au	Cubic close packing (ccp)	12
Li, Na, K, Rb, Cs	Body-centred cubic arrangement (bcc)	8

1.14.2 RELATIONSHIP BETWEEN FORMULA OF A COMPOUND AND NUMBER OF VOIDS FILLED

When particles are close packed resulting in either hcp or ccp structure, two types of voids are formed: tetrahedral voids and octahedral voids

$$\begin{aligned} \therefore \text{Number of close-packed particles} \\ &= \text{Number of octahedral voids (OVs)} \\ &= 2 \times \text{Number of tetrahedral void (TVs)} \end{aligned}$$

Number of effective atoms (Z_{eff}) in ccp and fcc

$$\begin{aligned} \text{Packing efficiency in hcp and ccp structures} &= \frac{\sqrt{2}}{6} \pi \times 4 / \text{unit cell} \\ &= 0.74 = 74\% \end{aligned}$$

Note: The calculation of packing efficient in ccp is similar to the packing efficiency in fcc [refer section 1.12(c)].

In ionic solids, the bigger ions (usually anions) form the close-packed structures and the smaller ions (usually cations) occupy, the voids. If the cations are small enough then tetrahedral voids are occupied, if bigger, then octahedral voids are occupied. Not all octahedral voids or tetrahedral voids are occupied. In a given

compound, the fraction of octahedral voids or tetrahedral voids that are occupied depends upon the chemical formula of the compound.

1.14.3 STACKING SEQUENCE

It is a sequence in which closest packing can exist.

In stacking sequence, the same layer cannot repeat just after a layer, i.e., A after A is restricted.

If carefully observed, a stacking sequence has fcc, hcp, and combination of fcc and hcp such that all are closely packed with the packing efficiency of 74%.

ILLUSTRATION 1.13

Select the close-packing arrangements in the following:

- a. ... ABABABA ... b. ... ABCABCABCA ...
c. ... ABABCABABC ... d. ... ACCBCABCABC ...

Sol. (a, b, c)

hcp, ccp, and their combination (hcp + ccp) are close-packed arrangements with packing efficiency of 74%.

1.14.4 LOCATION OF TETRAHEDRAL AND OCTAHEDRAL VOIDS

In a close-packed structure (ccp or fcc), there are both tetrahedral and octahedral voids. If there are N atoms or ions in the close packing, then

$$\text{Number of OV's} = N$$

$$\text{Number of TV's} = 2N$$

Location of Tetrahedral Voids

Consider a unit cell of ccp or fcc lattice [Fig. 1.44(a)]. The unit cell is divided into eight small cubes. Each small cube has atoms at alternate corners, i.e., four atoms in all. After joining them, a regular tetrahedron is formed. Thus, there is one tetrahedral void in each small cube and eight tetrahedral voids in total [Fig. 1.44(c)]. Each of the eight small cubes have one void in one unit cell of ccp lattice.

$$\therefore \text{Number of TV} = 8/\text{unit cell}$$

$$Z_{\text{eff}} \text{ in ccp or fcc unit cell} = 4$$

$$\text{Hence, number of TV} = 2 \times Z_{\text{eff}} \text{ in ccp or fcc unit cell.}$$

Moreover, in the fcc unit cell, two tetrahedral voids are formed on each of the four nonparallel body diagonals of the cube at a distance of $\sqrt{3}a/4$ from every corner along the body diagonal.

Alternatively, the centres of tetrahedral voids lie $1/4$ th distance of each body diagonal from one corner or $3/4$ th distance of each body diagonal from the other corner. [Figs. 1.44(c-e)].

Note: Body diagonal (AB) [Fig. 1.44(e)] = $\sqrt{3}a$

Distance between two tetrahedral voids ($A'B'$) is given as:

$$AB = AA' + BB' + A'B'$$

$$\sqrt{3}a = \frac{\sqrt{3}}{4}a + \frac{\sqrt{3}}{4}a + A'B'$$

$$\Rightarrow A'B' = \frac{1}{2} \times \sqrt{3}a = \frac{1}{2} \times \text{Body diagonal}$$

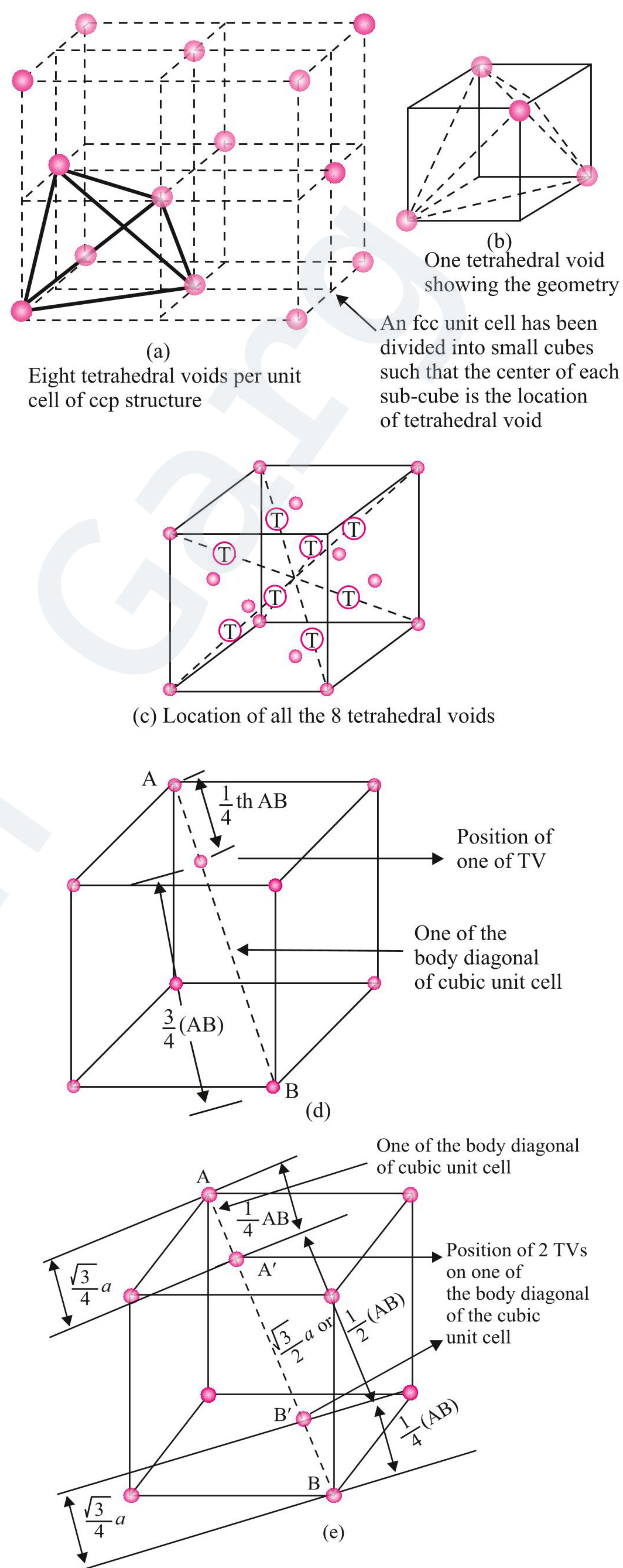


Fig. 1.44

$$\text{Nearest distance between 2 TV's} = \frac{\sqrt{3}}{2}a$$

Location of Octahedral Voids

Consider again a unit cell of ccp or fcc lattice [Fig. 1.45(a)]. The body centre of the cube C is not occupied but it is surrounded by six atoms on face centres [marked in Fig. 1.45(a) as 1 to 6]. On joining these face centres, an octahedron void is formed.

Thus, number of OV at the body centre of the cube = 1

Besides the body centre, there is one octahedral void at the centre of each of the 12 edges [Fig. 1.45(b)]. It is surrounded by six atoms, three belonging to the same unit cell (two on the corners and one on face centre), and three belonging to two adjacent unit cells.

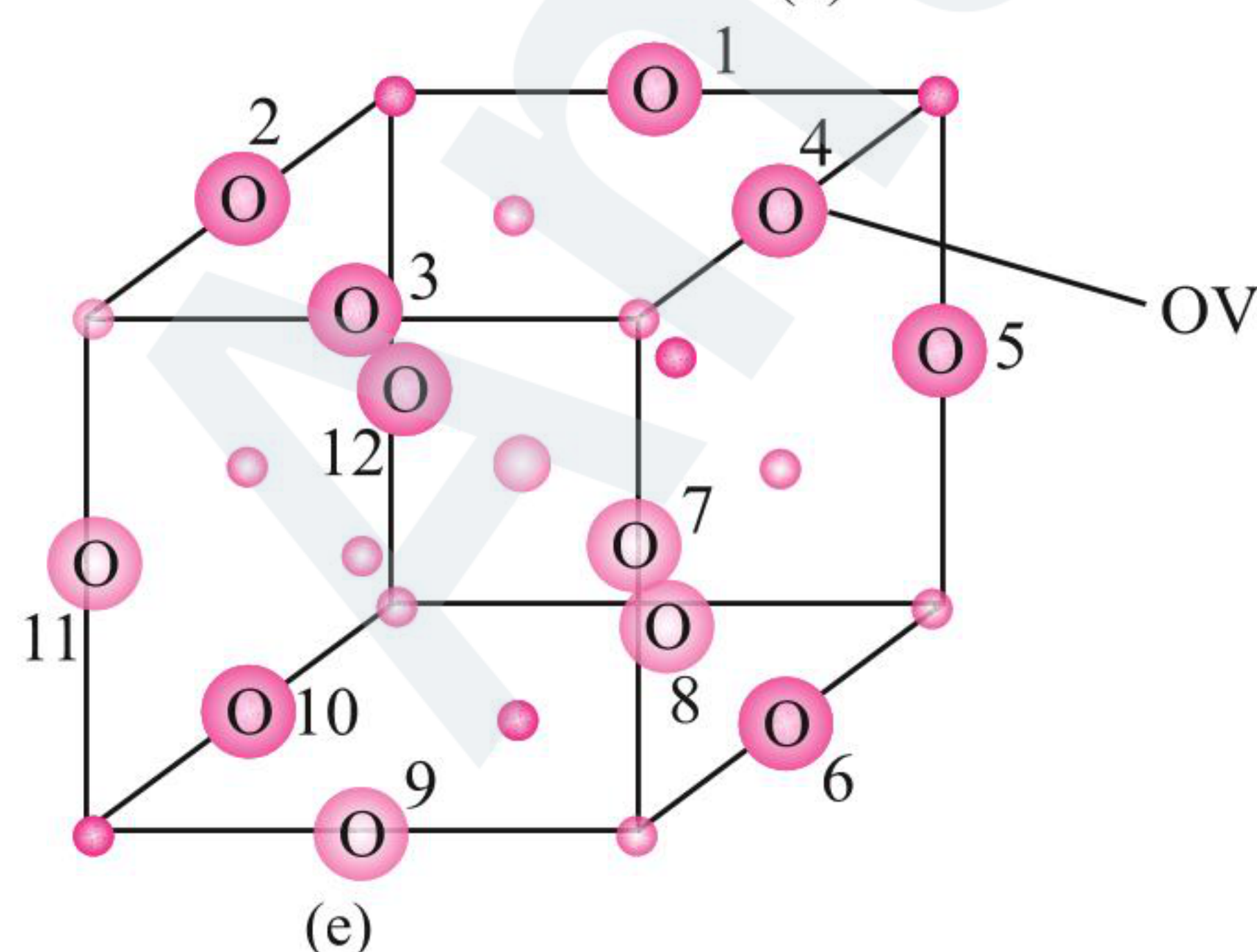
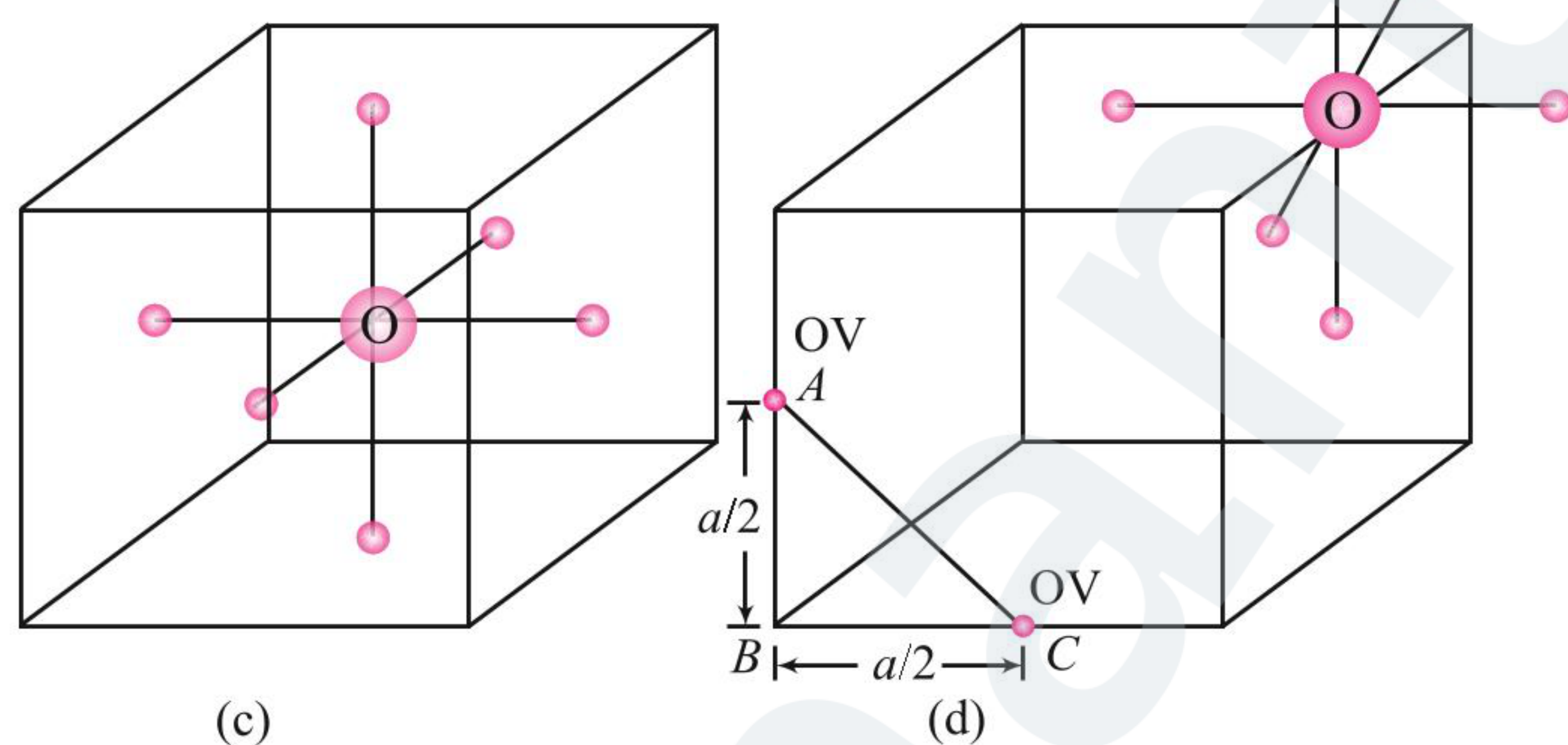
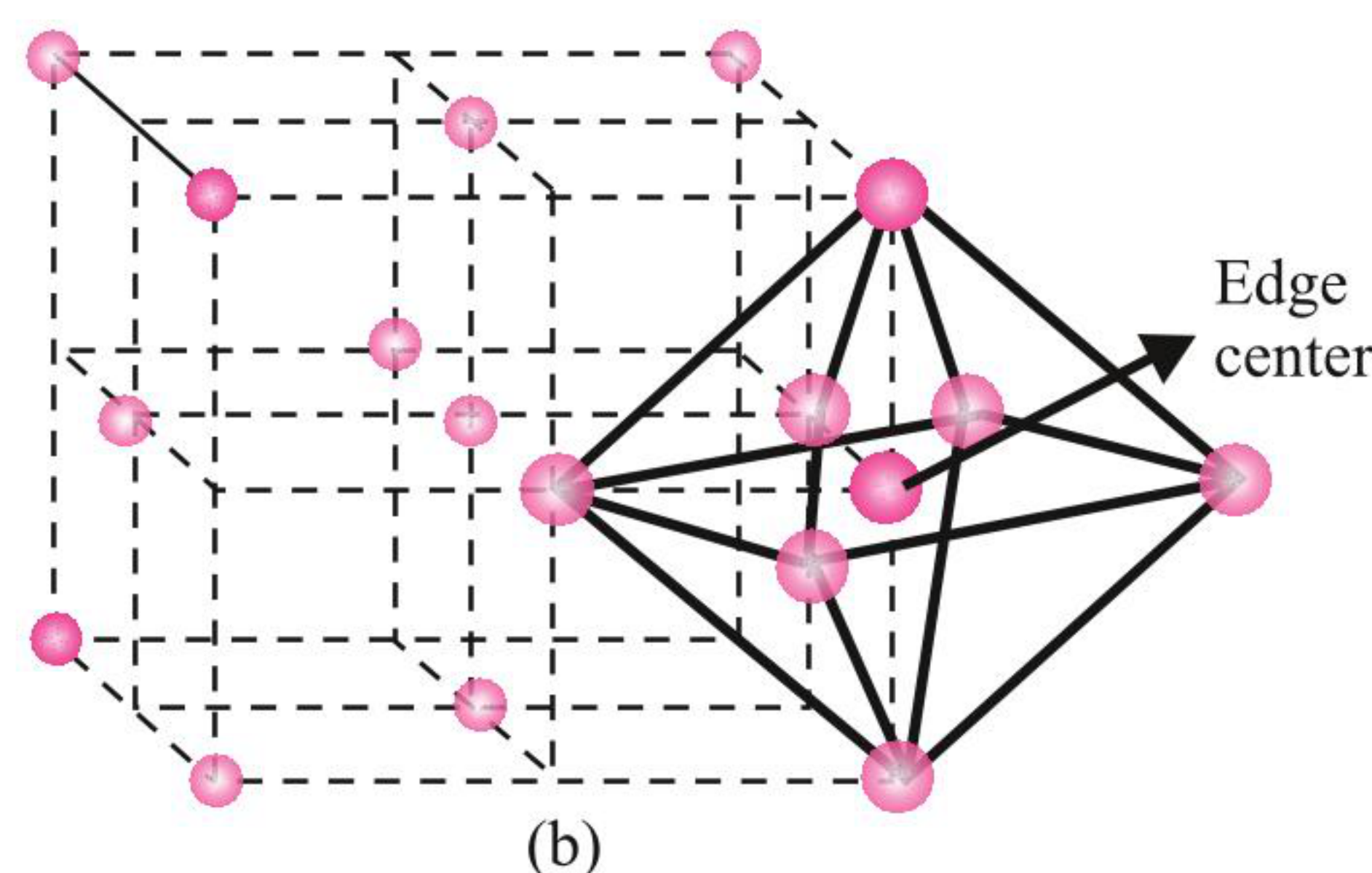
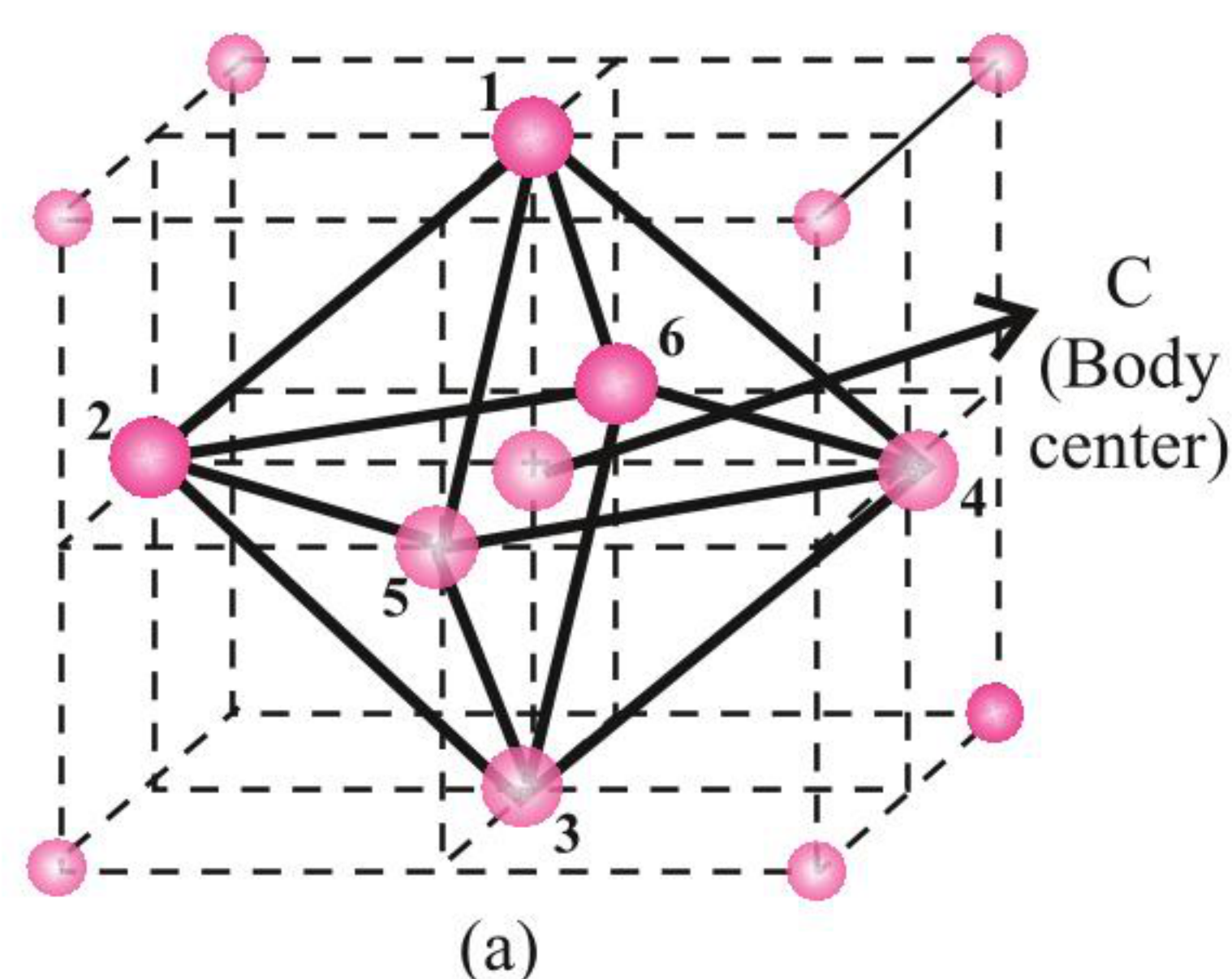


Fig. 1.45 Location of octahedral voids per unit cell of ccp or fcc lattice (a) at the body centre of the cube, (b) at the centre of each edge (only one such voids is shown), (c) octahedral void at the body centre (share by none), (d) octahedral void at the edge centre (shared by four unit cells), and (e) 12 octahedral voids at the edge centres

Nearest distance between 2 OV's [Fig. 1.45(d)]

$$(AC)^2 = (AB)^2 + (BC)^2 = \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 = \frac{a^2}{2} \therefore AC = \frac{a}{\sqrt{2}}$$

Since each edge of the cube is shared between four adjacent unit cells, so only 1/4th of each void belongs to a particular unit cell [Figs. 1.45(c-e)].

$\therefore$ OV at the body centre of the cube = 1

OV at the 12 edges of the cube and shared between four unit cells = $12 \times \frac{1}{4} = 3$

$\therefore$ Total number of OVs = 1 + 3 = 4

Z_{eff} in ccp or fcc structure = 4

$\therefore$ Number of OVs = Z_{eff} in ccp or fcc unit cell

ILLUSTRATION 1.14

A compound is formed by two elements X and Y. Atoms of the element Y (as anions) make ccp and those of element X (as cations) occupy all the octahedral voids. What is the formula of the compound?

Sol. The ccp lattice is formed by the element Y.

First method

$\therefore Z_{\text{eff}}$ of Y (as anions) = 4

Number of TVs = 8/unit cell

Number of OVs = 4/unit cell

Since all the OVs are occupied by X.

$\therefore$ Number of X (as cations) = 4.

$\therefore$ Formula = $X_4Y_4 = 4XY$

Second method

Let Z_{eff} of Y (as anions) = 1

Number of TVs = 2/atom or anion

Number of OVs = 1/atom or anion.

Since all the OVs are occupied by X.

$\therefore$ Number of X (as cations) = 1

$\therefore$ Formula = XY

ILLUSTRATION 1.15

Atoms of element B form hcp lattice and those of element A occupy two-thirds of tetrahedral voids. What is the formula of the compound formed by elements A and B?

Sol. The hcp lattice is formed by element B.

First method

$\therefore Z_{\text{eff}}$ of B (hcp lattice) = 6

Number of TV = 12/unit cell

Number of OV = 6/unit cell

Since element A occupies two-thirds of TVs

$\therefore$ Number of A = $\frac{2}{3} \times 12 = 8$

$\therefore$ Formula = $A_8B_6 = A_4B_3$

Second method

Let Z_{eff} of B = 1

Number of TV = 2/atom

Number of OV = 1/atom

$$\therefore \text{Number of A} = \frac{2}{3} \times \text{TV} = \frac{2}{3} \times 2 = \frac{4}{3}$$

$$\therefore \text{Formula} = \text{A}_{4/3}\text{B}_1$$

Simplifying: A_4B_3

ILLUSTRATION 1.16

An element has a bcc structure with a cell edge of 288 pm. The density of the element is 7.2 g cm^{-3} . How many atoms are present in 208 g of the element?

Sol. Volume of unit cell = $(288 \text{ pm})^3 = (288 \times 10^{-12} \text{ m})^3$
 $= (288 \times 10^{-10} \text{ cm})^3$
 $= 2.39 \times 10^{-23} \text{ cm}^3$

For bcc, $Z_{\text{eff}} = 2$

$$\therefore \rho = \frac{Z_{\text{eff}} \times A_w}{N_A \times a^3}$$

$$7.2 \text{ g cm}^{-3} = \frac{2 \times A_w}{6 \times 10^{23} \times 2.39 \times 10^{-23} \text{ cm}^3}$$

$$\therefore A_w/2 = 7.2 \times 6 \times 10^{23} \times 2.39 \times 10^{-23} \text{ g}$$

$$\therefore A_w = 7.2 \times 3 \times 2.39 \text{ g}$$

$$\therefore 7.2 \times 3 \times 2.39 \text{ g of element contains} = N_A \text{ atoms}$$

$$= 6 \times 10^{23} \text{ atoms.}$$

$$\therefore 208 \text{ g of the element contains} = \frac{6 \times 10^{23} \times 208}{7.2 \times 3 \times 2.39}$$

$$= 24.16 \times 10^{23} \text{ atoms}$$

Alternatively

$$\text{Volume of 208 g of the element} = \frac{\text{Mass}}{\text{Density}} = \frac{208 \text{ g}}{7.2 \text{ g cm}^{-3}}$$

$$= 28.88 \text{ cm}^3$$

Number of unit cells in this volume

$$= \frac{28.88 \text{ cm}^3}{2.39 \times 10^{23} \text{ cm}^3/\text{unit cell}}$$

$$= 12.08 \times 10^{23} \text{ unit cells}$$

Since each bcc cubic unit cell contains 2 atoms, therefore the total number of atoms in 208 g

$$= 2 (\text{atoms/unit cell}) \times 12.08 \times 10^{23} \text{ unit cells}$$

$$= 24.16 \times 10^{23} \text{ atoms}$$

ILLUSTRATION 1.17

X-ray diffraction studies show that copper crystallizes in an fcc unit cell with cell edge of $3.608 \times 10^{-8} \text{ cm}$. In a separate experiment, copper is determined to have a density of 8.92 g cm^{-3} . Calculate the atomic mass of copper.

Sol. In case of fcc lattice, number of atoms per unit cell, $Z = 4$ atoms

$$\therefore A_w = \frac{\rho N_A a^3}{Z_{\text{eff}}}$$

$$\frac{8.92 \text{ g cm}^{-3} \times 6.022 \times 10^{23} \text{ atoms mol}^{-1}}{4 \text{ atoms}} \times (3.608 \times 10^{-8} \text{ cm})^3$$

$$= 63.1 \text{ g mol}^{-1}$$

Atomic mass of copper = 63.1 u

ILLUSTRATION 1.18

Silver forms ccp lattice and X-ray studies of its crystals show that the edge length of its unit cell is 408.6 pm. Calculate the density of silver (atomic mass = 107.9 u).

Sol. Since, the lattice is ccp, the number of silver atoms per unit cell = $Z = 4$

Atomic mass of silver = 107.9 g mol⁻¹

$$= 107.9 \times 10^{-3} \text{ kg mol}^{-1}$$

Edge length of unit cell = $a = 408.6 \text{ pm} = 408.6 \times 10^{-12} \text{ m}$

$$\text{Density, } (\rho) = \frac{Z_{\text{eff}} \times A_w}{a^3 \times N_A}$$

$$= \frac{4 \times (107.9 \times 10^{-3} \text{ kg mol}^{-1})}{(408.6 \times 10^{-12} \text{ m})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}$$

$$= 10.5 \times 10^3 \text{ kg m}^{-3} = 10.5 \text{ g cm}^{-3}$$

ILLUSTRATION 1.19

Metallic gold crystallizes in the fcc lattice. The length of the cubic unit cell is $a = 4.242 \text{ \AA}$.

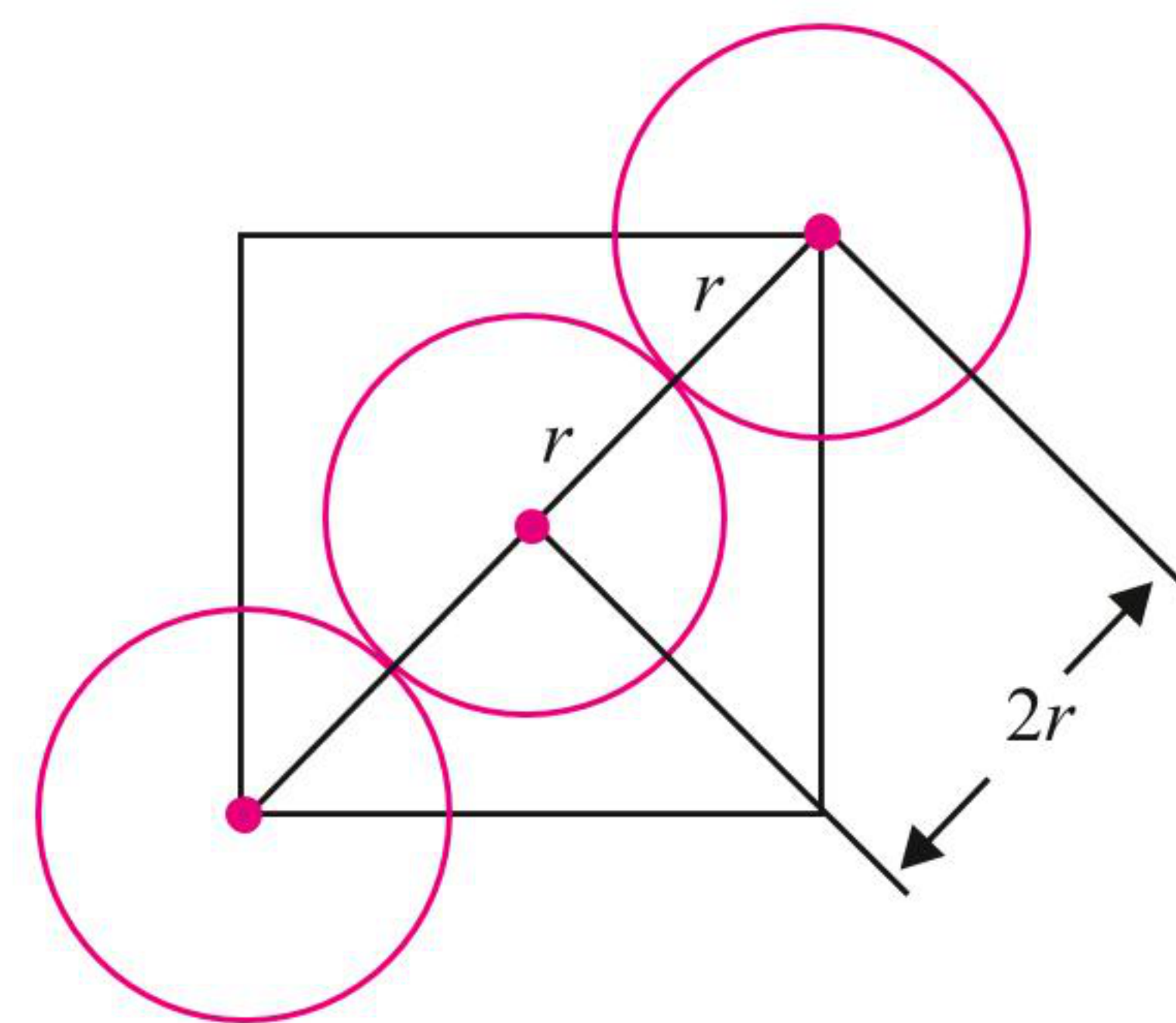
- What is the closest distance between gold atoms?
- How many “nearest neighbours” does each gold atom have at the distance calculated in (a)?
- What is the density of gold? (A_w of Au = 197.0 g mol^{-1})
- Prove that the packing factor for gold is 0.74.

Sol. In fcc, $Z_{\text{eff}} = 4$.

For fcc, atomic radius (r) = $\frac{a}{2\sqrt{2}}$

a. Closest distance between two Au atoms = $2r$

$$= 2 \times \frac{a}{2\sqrt{2}} = \frac{a}{\sqrt{2}} = \frac{4.242}{\sqrt{2}} = \frac{4.242}{1.414} = 3.0 \text{ \AA}$$



b. As the coordination number of fcc = 12.

So there are 12 nearest neighbours in all, the number expected for a close-packed structure.

$$\begin{aligned} \text{c. Density} = \rho &= \frac{Z_{\text{eff}} \times A_w}{N_A \times a^3} \\ &= \frac{4 \times 197 \text{ g}}{6 \times 10^{23} \times (3.0 \times 10^{-8} \text{ cm})^3} \\ &= 48.64 \text{ g cm}^{-3} \end{aligned}$$

$$\text{d. Packing factor for fcc lattice} = \frac{\sqrt{2}}{6} \pi = 0.7404$$

[For proof refer to section 1.12(c)]

ILLUSTRATION 1.20

If the radius of an atom of an element is 75 pm and the lattice type is body-centred cubic, what is the edge length of the unit cell?

$$\begin{aligned} \text{Sol. For BCC, } r &= \frac{\sqrt{3}}{4} a \\ \text{or } a &= \frac{4r}{\sqrt{3}} = \frac{4 \times 75}{1.732} = 173.2 \text{ pm} \end{aligned}$$

ILLUSTRATION 1.21

The radius of an atom of an element is 500 pm. If it crystallizes as a face-centred cubic lattice, what is the length of the side of the unit cell?

$$\begin{aligned} \text{Sol. For fcc, } r &= \frac{a}{2\sqrt{2}} \\ \text{or } a &= 2\sqrt{2} r = 2 \times 1.414 \times 500 \text{ pm} = 1414 \text{ pm} \end{aligned}$$

ILLUSTRATION 1.22

Sodium has a bcc structure with nearest neighbour distance of 365.9 pm. Calculate its density. (Atomic mass of sodium = 23)

Sol. For the bcc structure, nearest neighbour distance (d) is related to the edge (a) as

$$\begin{aligned} d &= \frac{\sqrt{3}}{2} a \\ \text{or } a &= \frac{2}{\sqrt{3}} d = \frac{2}{1.732} \times 365.9 = 422.5 \text{ pm} \end{aligned}$$

For bcc structure, $Z_{\text{eff}} = 2$

For sodium, $A_w = 23$

$$\begin{aligned} \therefore r &= \frac{Z_{\text{eff}} \times A_w}{a^3 \times N_A \times 10^{-30}} \\ &= \frac{2 \times 23}{(422.5)^3 \times (6.02 \times 10^{23}) \times 10^{-30}} \text{ g cm}^{-3} = 1.51 \text{ g cm}^{-3} \end{aligned}$$

ILLUSTRATION 1.23

A face-centred cubic element (atomic mass 60) has a cell edge of 400 pm. What is its density?

Sol. For the face-centred cubic, $Z_{\text{eff}} = 4$

$$\rho = \frac{Z_{\text{eff}} \times A_w}{a^3 \times N_A \times 10^{-30}} \text{ g cm}^{-3}$$

$$= \frac{4 \times 60}{(400)^3 \times (6.02 \times 10^{23}) \times 10^{-30}} = 6.23 \text{ g cm}^{-3}$$

ILLUSTRATION 1.24

Xenon crystallizes in the face-centred cubic lattice and the edge of the unit cell is 620 pm. What is the nearest neighbour distance and what is the radius of xenon atom?

Sol. Here $a = 620 \text{ pm}$, $d = ?$, $r = ?$

For the face-centred cubic lattice,

$$d = \frac{a}{\sqrt{2}} = \frac{620 \text{ pm}}{1.414} = 438.5 \text{ pm}$$

$$r = d/2 = 438.5/2 = 219.25 \text{ pm}$$

1.15 STRUCTURE OF IONIC CRYSTALS

In ionic crystals, there are two types of ions, cations and anions. Both have different sizes and charges. Due to the attraction between opposite charges, there is a tendency of one type of charge to surround ions of the opposite charge. Due to difference in ionic sizes, the structure of a given solid is determined by geometrical considerations during the packing of ions of different sizes.

The cation is assumed to be the smaller ion. The number of anions surrounding a central cation is called the *coordination number* or *ligancy*. The ligancy is a function of the sizes of the ions. The ionic radius ratios of cation (r_c) and anion (r_a) is very important in the determination of the crystal structures of an ionic substance.

If anions are arranged around a cation and vice versa and keeping the size of the cation same, as the size of the anion decreases, the ligancy (or coordination number) increases (Fig. 1.46).

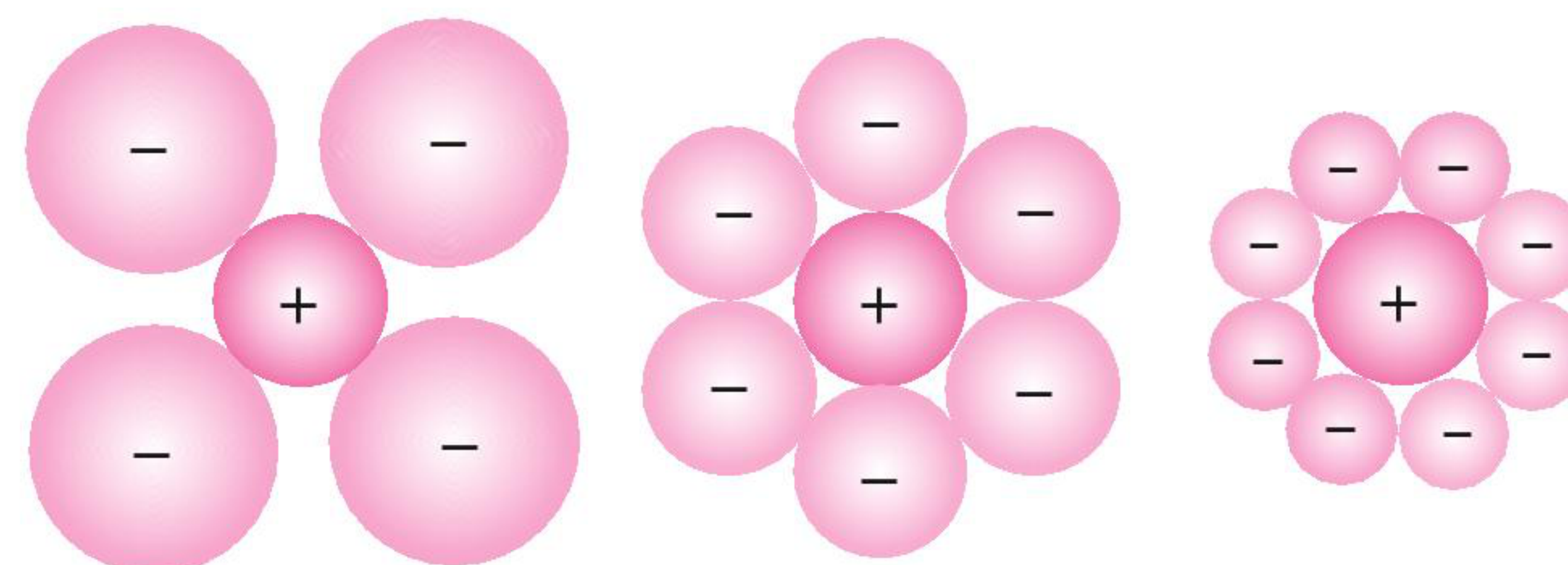


Fig. 1.46 Illustration of the importance of ionic ratio in packing (as the ratio r_c/r_a increases more number of anions can be arranged around cations)

1.15.1 RADIUS RATIO RULES

Following conditions must be satisfied simultaneously during the stacking of ions of different sizes in an ionic crystal:

- An anion and a cation are assumed to be hard spheres always touching each other.
- Anions generally will not touch but may be close enough to be in contact with one another in a limiting situation.
- A cation should surround itself with as many anions as possible. Each ion tends to surround itself with as many ions of opposite sign as possible to reduce the potential energy. This tendency promotes the formation of close-packed structures.

When a cation is very small compared to an anion, it is easily seen that only two anions can be neighbours to the cation in order to satisfy all the above three conditions. Consider the configuration as shown in Fig. 1.47(a) below. Here, the three surrounding anions are touching one another as well as the central cation.

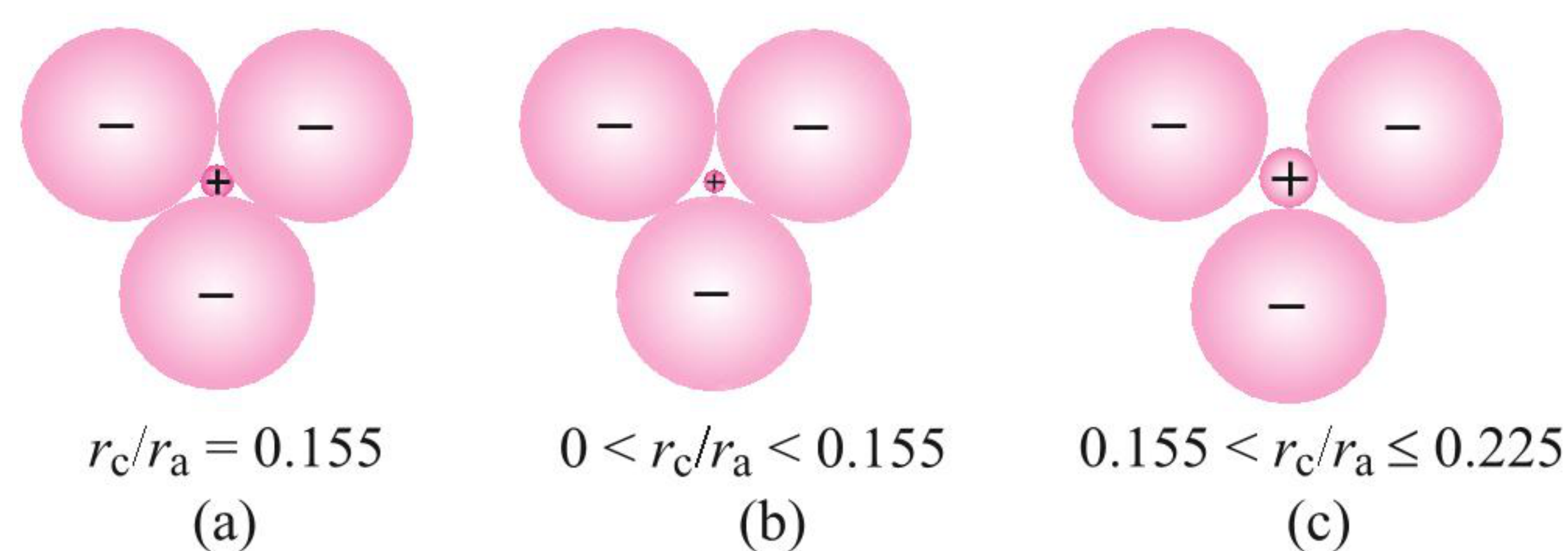


Fig. 1.47 Triangular coordination of anions around a central cation:
 (a) critical configuration, (b) unstable configuration, and
 (c) stable (but not critical) configuration

The ratio of the cation to anion radius r_c/r_a for this configuration is 0.155, which can be worked out from the simple geometry (see Fig. 1.48). The triangular arrangement in (a) is one of the limiting situations. The radius ratio is said to be a critical value because for the value of r_c/r_a smaller than 0.155, the central cation will rattle in the hole and not touch all the three anions at the same time, as illustrated in (b). This violates condition (a) above and leads to

instability. When the radius ratio is less than 0.155, then the only way to satisfy all three conditions is to reduce the number of anions to 2. For values of r_c/r_a slightly greater than 0.155, all the anions touch the central cation but do not touch one another, as shown in (c). All three conditions of stability are still satisfied. This situation will prevail till the radius ratio increases to 0.225, the next higher critical value corresponding to a tetrahedral (four) coordination. At $r_c/r_a = 0.225$, the four surrounding anions touch one another and also the central cation. This configuration is same as that obtained by fitting the largest possible sphere in the tetrahedral void of a close-packed structure (see Fig. 1.49).

A ligancy of 5 does not satisfy all the three conditions for stable configuration because it is always possible to have six anions as an alternative to any arrangement that contains five anions, without a change in the radius ratio. The critical condition for octahedral (six) coordination occurs at $r_c/r_a = 0.414$, which is same as the size of the octahedral void in a close-packed structure. Ligancies of 7, 9, 10, and 11 are again not permissible.

The radius ratio ranges in which different values of ligancy are obtained are summarized in Table 1.11. At the end of the table, the limiting case of $r_c/r_a = 1$ is identified with configurations of close packing of equal-sized spheres.

Table 1.11 Ligancy as a function of radius ratio in 1 : 1 or AB-type structure

S. No.	Ligancy or coordination number	Range of radius ratio (r^+/r^-)	Configuration	Structure type	Examples
1.	2	$0.0 < \frac{r^*}{R} < 0.155$	Linear	—	—
2.	3	$0.155 \leq \frac{r}{R} < 0.225$	Triangular	—	—
3.	4	$0.225 \leq \frac{r}{R} < 0.414$	Tetrahedral	ZnS	CuCl, CuBr, CuI, BaS, HgS
4.	6	$0.414 \leq \frac{r}{R} < 0.732$	Octahedral	NaCl	MgO, NaBr, CaS, MnO, KBr, CaO
5.	8	$0.732 \leq \frac{r}{R} < 1.0$	Cubic	CsCl	CsI, CsBr, TlBr, NH ₄ Br
6.	12	$\frac{r}{R} = 1.0$	fcc or hcp	—	—

* r = radius of cation; R = radius of anion

Note: There are exceptions for each type of structure, e.g., BeS ($r_c/r_a = 0.19$) has ZnS (sphalerite) type structures; LiI ($r_c/r_a = 0.34$), LiBr ($r_c/r_a = 0.38$), KCl ($r_c/r_a = 0.77$), RbCl ($r_c/r_a = 0.83$), BaO ($r_c/r_a = 0.97$) have NaCl-type or rock salt type structure.

Critical Radius Ratio for Triangular Coordination

The critical condition for triangular coordination is shown in Figure 1.56. The three anions touch one another as well as the central cation. From the simple geometry, we can write:

In $\triangle ABC$,

$$\cos 30^\circ = \frac{\text{Base}}{\text{Hypotenuse}} = R/R + r$$

$$(R + r) \cos 30^\circ = R$$

$$\Rightarrow R + r = \frac{2}{\sqrt{3}} R \quad (\because \cos 30^\circ = \sqrt{3}/2)$$

$$\Rightarrow \frac{r}{R} = \frac{2}{\sqrt{3}} - 1 = 0.155$$

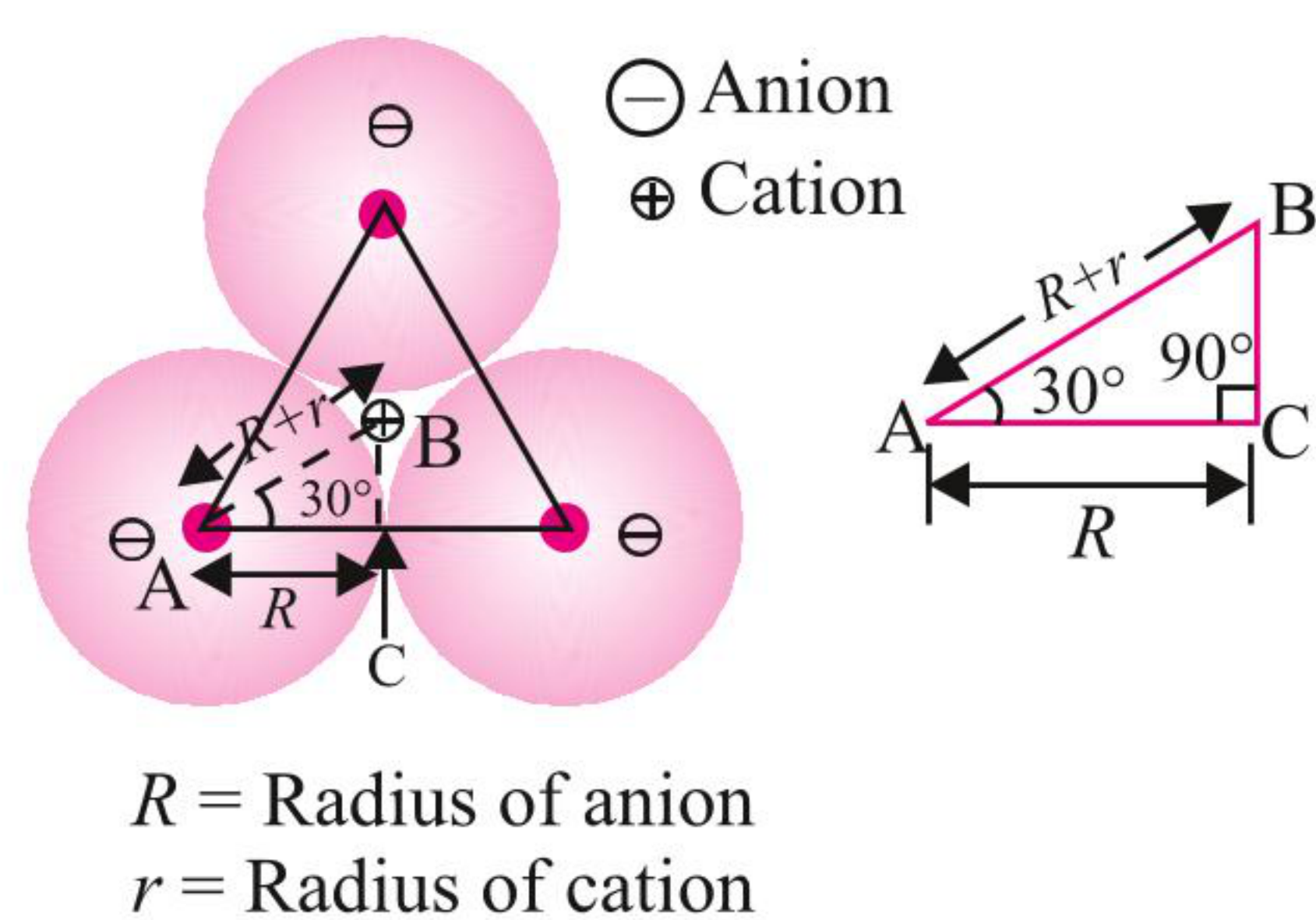


Fig. 1.48

Critical Radius Ratio for Tetrahedral Coordination or Relation Between Radius (r) of the TV and Radius (R) of the Atoms in Close-Packed Structures

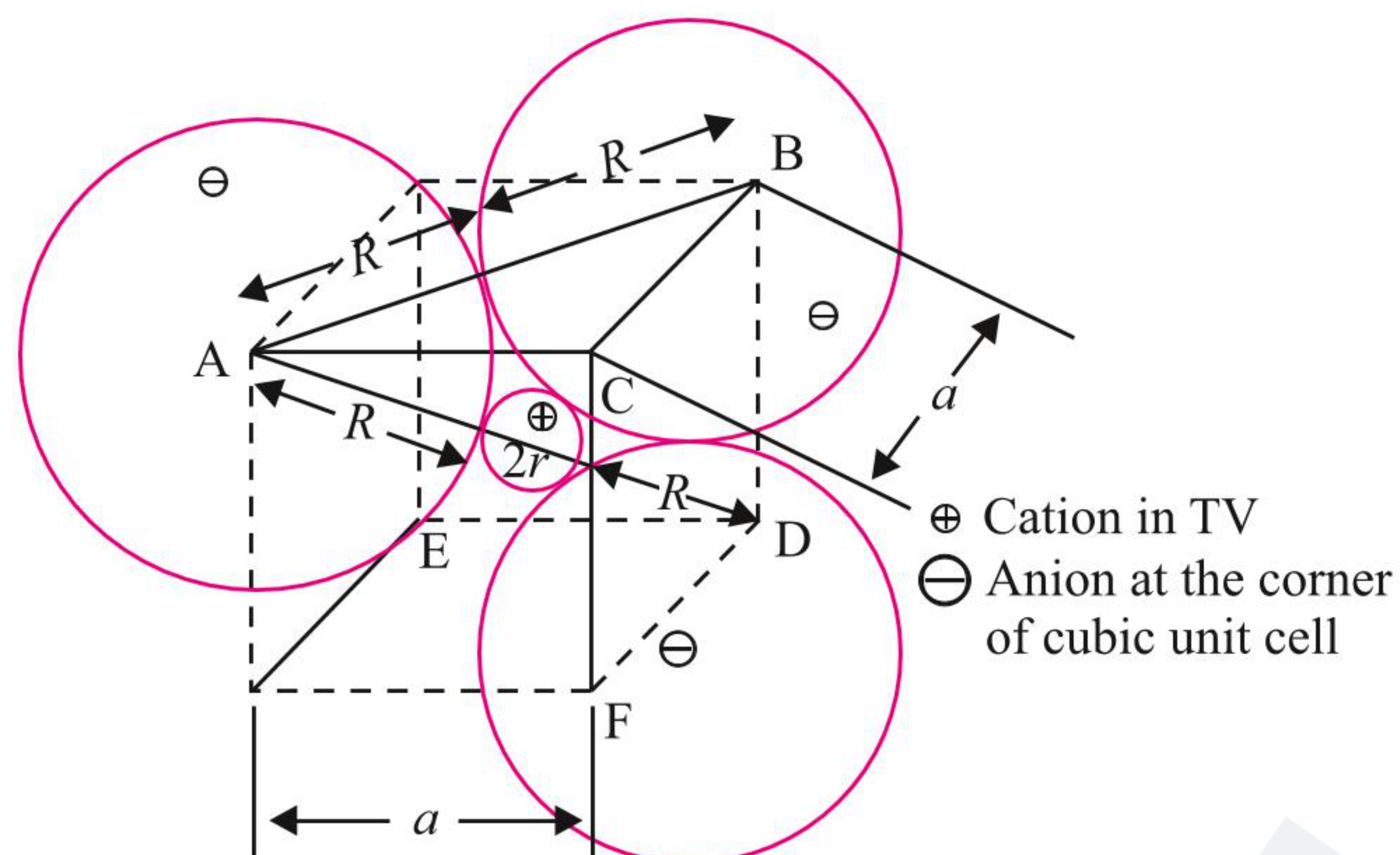


Fig. 1.49

The anions touch each other as well as the central cation. Let r is the radius of TV (cation), R is the radius of anions, and a is the edge length of the cubic unit cell.

From the right-angled triangle ABC, face diagonal (AB) is

$$AB = \sqrt{(AC)^2 + (BC)^2} = \sqrt{a^2 + a^2} = \sqrt{2}a$$

Since anions at A and B are actually touching each other in the close packing, face diagonal (AB) = $2R$.

$$\text{Hence, } 2R = \sqrt{2}a \text{ or } R = \frac{1}{\sqrt{2}}a \quad \dots(i)$$

Again from the right-angled triangle ABD,

$$\begin{aligned} \text{Body diagonal (AD)} &= \sqrt{(AB)^2 + (BD)^2} \\ &= \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a \end{aligned}$$

$$\therefore AD = 2(R + r) = \sqrt{3}a$$

$$\text{Hence, } (R + r) = \frac{\sqrt{3}}{2}a \quad \dots(ii)$$

Dividing Eq. (ii) by Eq. (i), we get

$$\frac{(R + r)}{R} = \frac{\sqrt{3}a/2}{a/\sqrt{2}} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\text{or } 1 + \frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\begin{aligned} \text{or } \frac{r}{R} &= \frac{\sqrt{3}}{\sqrt{2}} - 1 \\ &= \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.732 - 1.414}{1.414} = 0.225 \end{aligned}$$

$$\text{or } r = 0.225R \quad \left(\begin{array}{l} \text{Radius of TV} \\ \text{i.e., cation} \end{array} \right) = \left(\begin{array}{l} 0.225 \text{ radius} \\ \text{of the anion} \end{array} \right)$$

$$\text{or } r_c = 0.225r_a$$

Critical Radius Ratio for Octahedral Coordination or Relation Between Radius (r) of the OV and Radius (R) of the Atoms in Close-Packed Structures

The anions touch one another as well as the central cation present in OV. A sphere above and a sphere below this small cation (sphere) have not been shown in Fig. 1.50.

From right-angled ABC,

$$(BC)^2 = (AB)^2 + (AC)^2$$

$$\begin{aligned} (2R)^2 &= (R + r)^2 + (R + r)^2 \\ &= 2(R + r)^2 \end{aligned}$$

$$\text{or } \frac{(2R)^2}{2} = (R + r)^2$$

$$\text{or } (\sqrt{2}R)^2 = (R + r)^2 \Rightarrow \sqrt{2}R = R + r$$

$$\therefore r = \sqrt{2}R - R = R(\sqrt{2} - 1)$$

$$= R(1.414 - 1) = 0.414R$$

$$\therefore \text{Radius } (r) \text{ of OV} = 0.414R$$

Alternatively

$$(2r + 2R) \cos 45^\circ = 2R \Rightarrow r/R = \sqrt{2} - 1 = 0.414$$

In case of ionic compounds, anions are usually present in close packing and cations occupy the voids, we can also write

a. For cations occupying TVs, $r_c = 0.225r_a$.

b. For cations occupying OVs, $r_c = 0.414r_a$.

Hence, a TV is much smaller than the OV. Moreover, the maximum size of the cation occupying the void is $0.414R$. If the smaller spheres (i.e., cation) to occupy the voids have size larger than this, the arrangement will no longer be close packed.

Critical Radius Ratio for Body-Centred Co-ordination or Relation Between Radius (r) of the Body-Centred Void and Radius (R) of the Atoms

The critical condition for cubic void is shown in Fig. 1.51. The anions touch one another (as in sc) as well as the central cation. From the simple geometry, we can write

$$a = 2R \text{ and } \sqrt{3}a = 2R + 2r$$

$$\Rightarrow \frac{r}{R} = \sqrt{3} - 1 = 0.732 \Rightarrow r = 0.732R$$

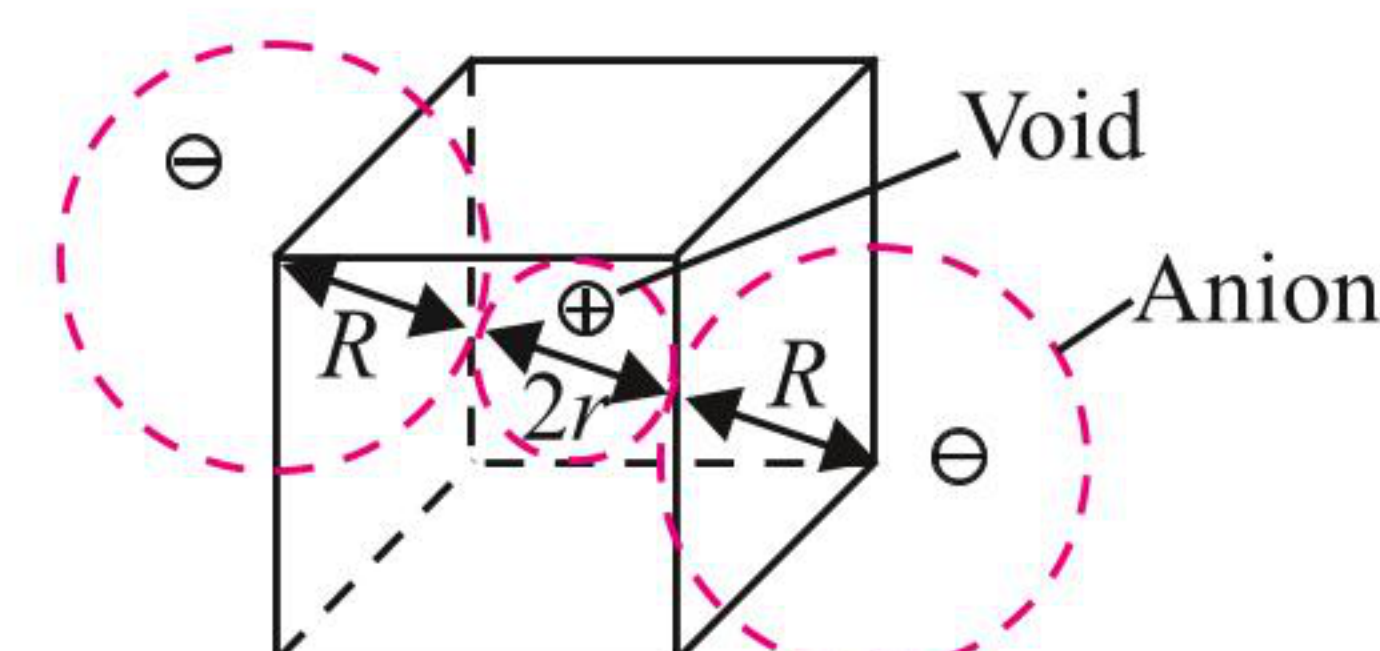


Fig. 1.51

1.15.2 COORDINATION NUMBER IN SOME IONIC COMPOUNDS

The ligancy rules outlined above are obeyed in a number of cases. For example, in the NaCl crystal, the ratio $r_{\text{Na}^+} / r_{\text{Cl}^-} = 0.54$, which lies between 0.414 and 0.732. As listed in Table 1.11, the predicted ligancy is 6. The octahedral geometry of six chlorine ions surrounding a central cation is experimentally observed. In MgO, $r_{\text{Mg}^{2+}} / r_{\text{O}^{2-}} = 0.59$ and again the octahedral coordination is observed. In CsCl, $r_{\text{Cs}^+} / r_{\text{Cl}^-} = 0.73$, it is difficult to predict whether a six-fold or an eight-fold coordination will occur. It so turns out that the eight-fold coordination is observed. In this case, that is, every cesium cation is surrounded by eight chlorine anions.

The Si–O bond in silica as well as in silicates is about 50% ionic and 50% covalent. Here, the central silicon cation is surrounded by four oxygen anions located at the corners of a regular tetrahedron. This arrangement satisfies both the ligancy rules (as $r_c/r_a = 0.29$, the tetrahedral coordination is predicted from Table 1.11, as well as the orientation relationships of sp^3 bonds).

The stability criteria listed above for predicting the ligancy may not always be valid. If the directional characteristics of bonding persist to any significant degree, the considerations based on the radius ratio alone will not lead to the correct prediction of ligancy. In the above-discussed example of Si–O coordination, the radius ratio criterion and the bond angle requirement happen to coincide. In ZnS, where the bond is more covalent than ionic, the ligancy predicted from $r_{\text{Zn}^{2+}}/r_{\text{S}^{2-}} = 0.48$ is octahedral. Yet the four-fold coordination characteristic of (sp^3) bonding is observed.

In the formation of ionic crystals, the ligancy rules described above determine the local packing around a cation. The long-range arrangement of ions in the crystal is dependent on the following factors:

- In the crystal, the *overall electrical neutrality* should be maintained, whatever be the net charge on a local group of a cation and surrounding anions. For example, in NaCl, where a cation is surrounded by six anions, the net charge on NaCl_6 is 5. Evidently, this has to be neutralized in the long-range arrangement.
- The ionic bond being non-directional, the ions are packed as closely as possible in the crystal, consistent with the local coordination.

When the cation charge is not more than 2 or at best 3 and when the radius ratio is in the range 0.414–0.732, the crystal structure can be described as fcc or hcp packing of anions with the cations occupying all or part of octahedral voids in the structure. The fraction of octahedral voids that are filled depends on the number of cations to anions in the chemical formula. Thus, for the rock salt (NaCl) structure, adopted by hundreds of binary ionic compounds, $r_{\text{Na}^+} / r_{\text{Cl}^-} = 0.54$ and the anion packing is fcc with all octahedral voids filled with sodium cations. Note that there is one octahedral void per sphere in a close-packed array. A unit cell of NaCl crystal is shown in Fig. 1.52, with the larger chlorine ions occupying the corner and face-centred cubic positions and the sodium ions in the octahedral voids. The octahedral positions are at the body centre and at the

midpoints of the cube edges. Note that unlike in the monoatomic fcc crystal, the chlorine ions do not touch one another along the face diagonal. This is so because the radius ratio of 0.54 is greater than the size of the octahedral void in a close-packed structure, which is 0.414. The fcc close packing is “opened up” here to the extent necessary to accommodate the sodium cations in the octahedral voids.

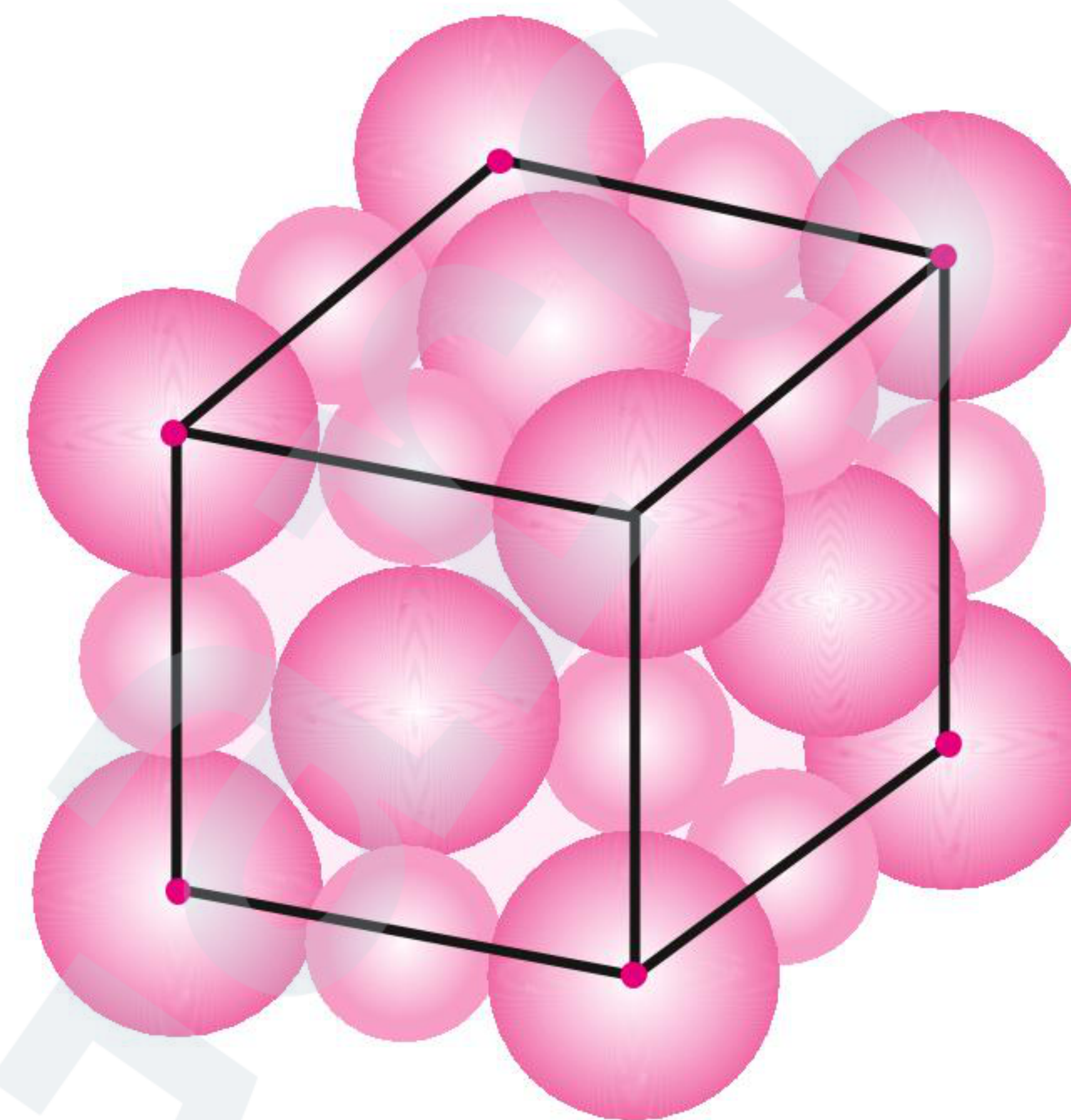


Fig. 1.52 A unit cell of NaCl with Cl^- at fcc positions and Na^+ ions in the octahedral voids

As the fcc positions and octahedral void centres are interchangeable like the body centre and body corners in the bcc cell, the NaCl structure can also be described as two interpenetrating monoatomic fcc cells, one corresponding to the anions and the other to the cations. The basis of the NaCl structure is one sodium ion plus one chlorine ion. The sum of their radii, $r_{\text{Na}^+} + r_{\text{Cl}^-} = a/2$, where a is the lattice parameter.

When r_c/r_a is in the range of 0.7312 to 1, an eight-fold coordination is observed. CsCl with $r_{\text{Cs}^+}/r_{\text{Cl}^-} = 0.91$ is a typical example of this structure. The cesium ions are at the body centre and the chlorine ions are at body corners. The space lattice is simple cubic, with a basis of one cesium ion plus one chlorine ion per lattice point.

1.16 STRUCTURES OF SIMPLE IONIC COMPOUNDS

Simple ionic compounds are the compounds of the type AB or AB_2 where A and B represent the positively and negatively charged ions, respectively. It is more difficult to describe the structures of even these simple ionic compounds as compared to those of the elements. This is because an element consists of only one type of atoms, all of which occupy the lattice points, e.g., in case of copper which is face-centred cubic (fcc), all lattice points are occupied by copper atoms. On the other hand, in case of even simple ionic compounds, the arrangement of both A and B ions has to be described, as given below.

1.16.1 SIMPLE IONIC COMPOUNDS OF TYPE AB

Ionic compounds of the type AB means compounds having positively and negatively charged ions in the ratio 1 : 1. These compounds have any one of the following three types of structures:

- Rock salt (NaCl) type structure
- Caesium chloride (CsCl) type structure
- Zinc blende (ZnS) or sphalerite type structure

The main features of each of these structures are discussed below.

Rock Salt (NaCl) Type Structure

The structure of NaCl is as shown in Fig. 1.53. The main features of this structure are as follows:

- It has a face-centred cubic (fcc) arrangement (also called cubic close packing, i.e., ccp) in which Cl^- ions occupy the corners and face centres of the cube while Na^+ ions are present at the body centre and edge centres.

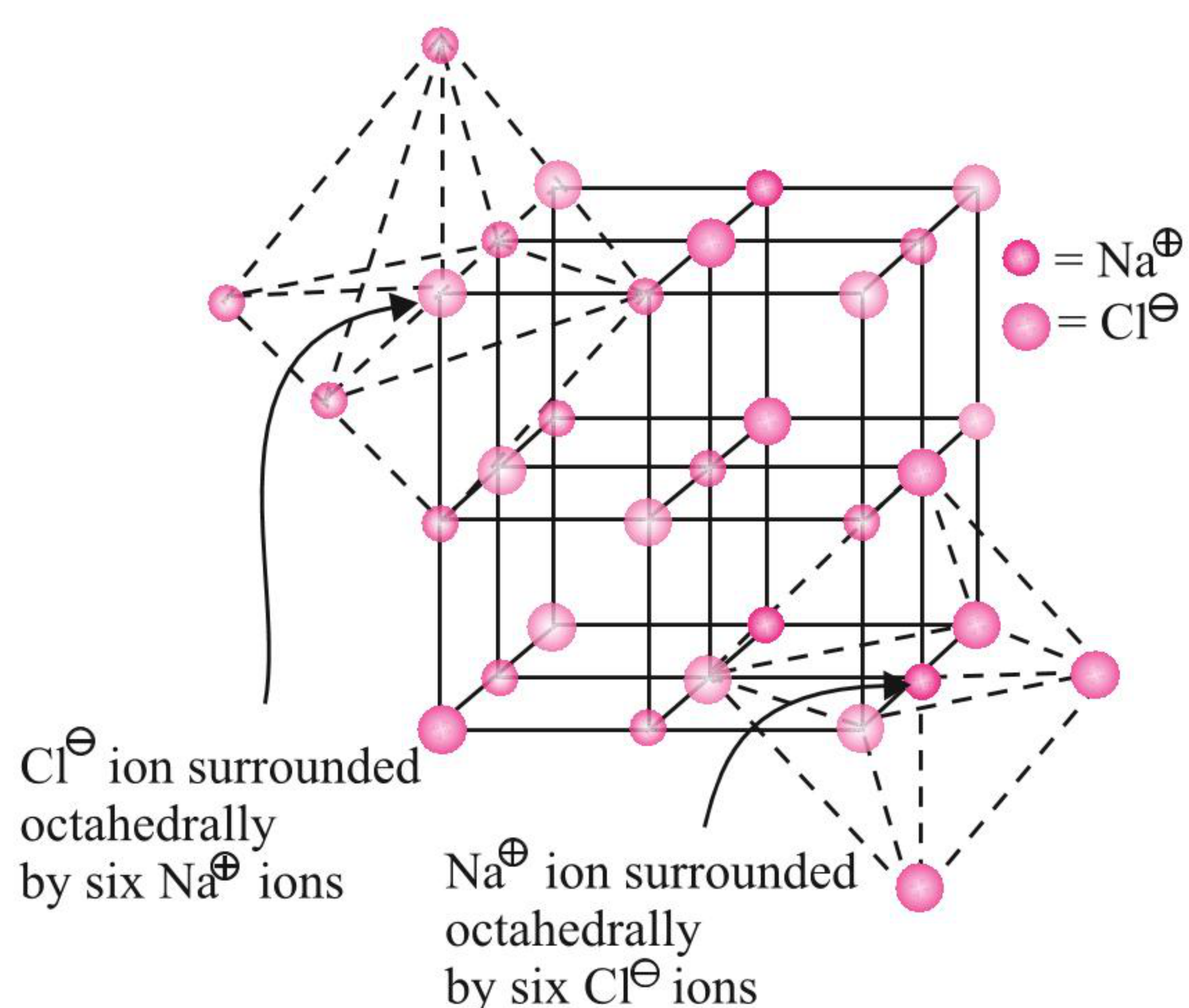


Fig. 1.53 NaCl structure

- Each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. In other words, the Na^+ ions as well as Cl^- ions have coordination number of 6, i.e., this structure has 6 : 6 coordination (i.e., Cl^- ions being larger in size are present in the close packing while Na^+ ions are present in all the octahedral voids. Further, for exact fitting of cations and anions, the radius ratio r_+/r_- should be 0.414. The actual value of $r_{\text{Na}^+}/r_{\text{Cl}^-} = 0.525$. Hence, to accommodate large Na^+ ions, Cl^- ions move apart slightly, i.e., they do not touch each other. Hence, it forms an expanded face-centred lattice).
- A unit cell of NaCl consists of four NaCl units, i.e., four Na^+ ions and four Cl^- ions as calculated below.
Eight Cl^- ions are present on the corners and six Cl^- ions on the faces so that Cl^- ions per unit cell = $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$.
Similarly, 12 Na^+ ions are present on the edges and one within the body so that Na^+ ion per unit cell = $\frac{1}{4} \times 12 + 1 = 4$.

A few examples of the compounds having structure similar to that of NaCl are as follows:

- Halides of alkali metals (except those of cesium) and that of ammonium
- Oxides and sulphides of alkaline earth metals (except BeS)
- Halides of silver (except silver iodide)

Caesium Chloride (CsCl) Type Structure

The structure of CsCl is as shown in Figs. 1.54(a) and 1.54(b).

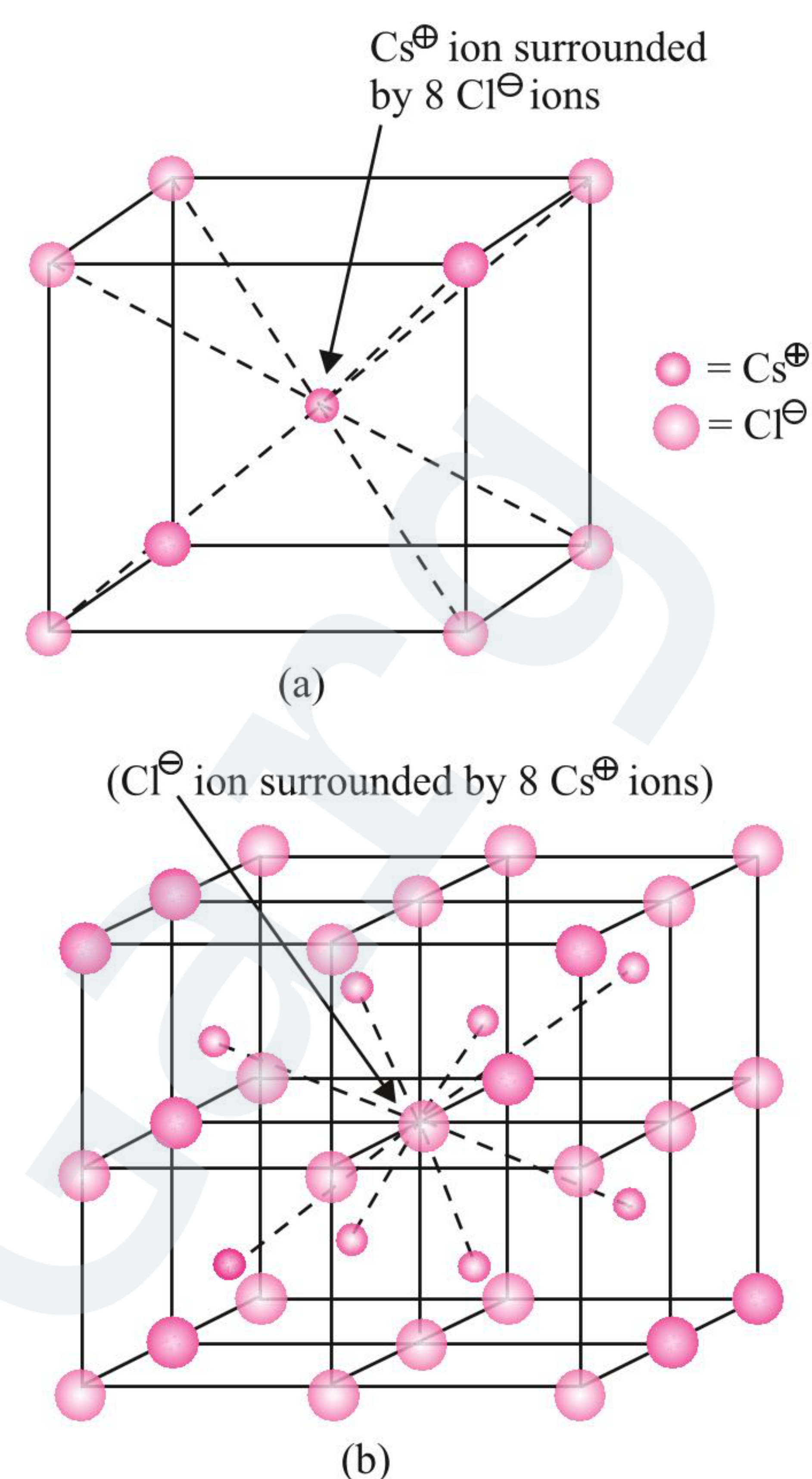


Fig. 1.54 (a) A unit cell of CsCl structure; and (b) the concept of reversibility in the case of CsCl crystal such that Cl^- lies in the simple cubic of Cs^+

The main features of this structure are as follows:

- It has body-centred cubic (bcc) arrangement.
- Each Cs^+ ion is surrounded by eight Cl^- ions and each Cl^- ion is surrounded by eight Cs^+ ions, i.e., this structure has 8 : 8 coordination.
- A unit cell of CsCl consists of only one unit of CsCl, i.e., one Cs^+ ion and one Cl^- ion (because each ion present at the corner is shared by eight unit cells) [The ratio $r_{\text{Cs}^+}/r_{\text{Cl}^-} = 0.93$ which is greater than expected for exact fitting (0.732)].

A few examples of compounds having CsCl structure are: CsBr, CsI, CsCN, TlCl, TlBr, TlI, and TlCN.

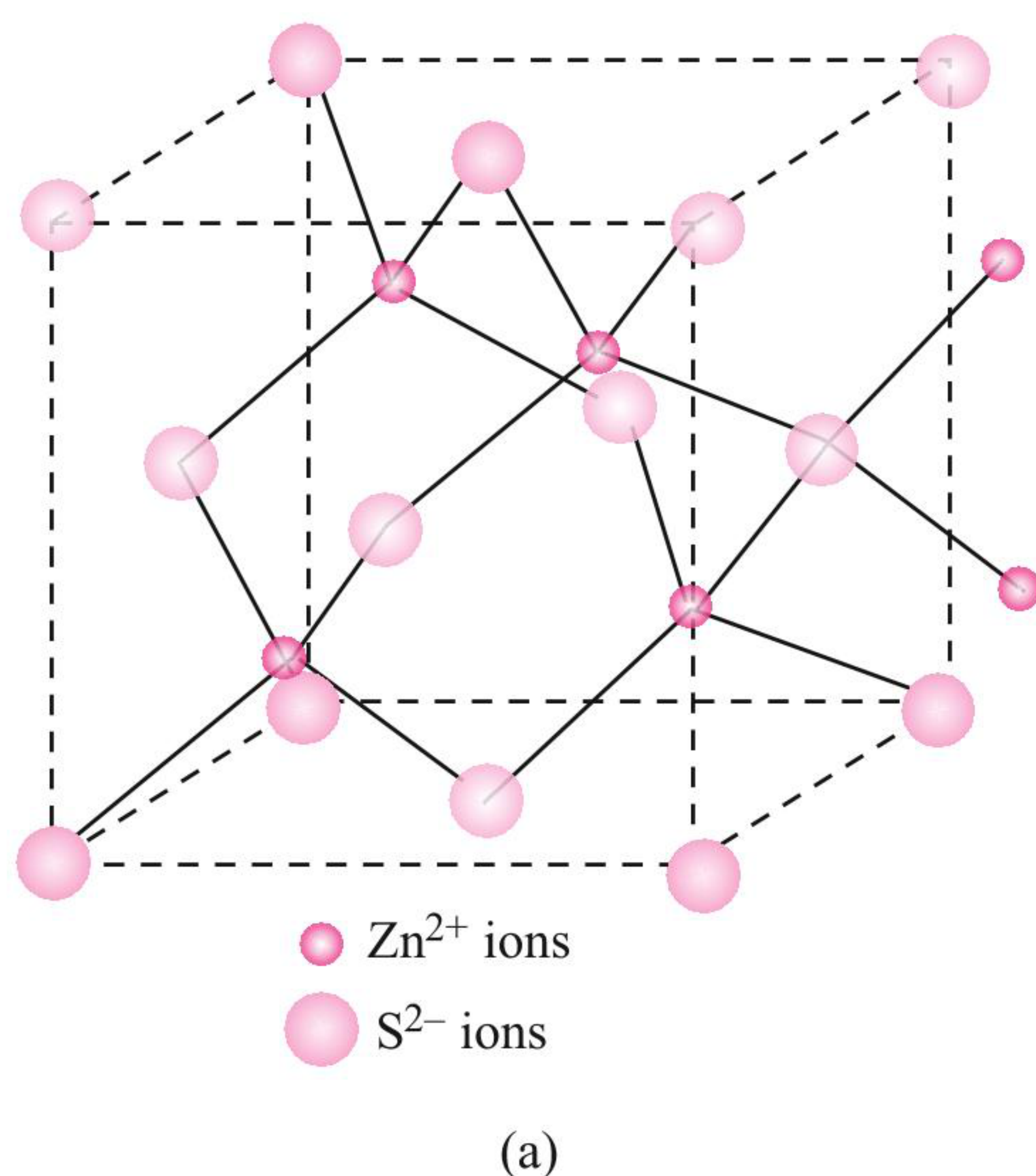
Zinc Blende (ZnS) Type Structure

The structure of ZnS is as shown in Fig. 1.55(a). It exists in two different forms, zinc blende and wurtzite. Both are 4 : 4 structures. The main features of this structure are as follows:

- The arrangement as possessed by ZnS is called cubic close packing (ccp) in which S^{2-} ions are present at the corners as well as at the centre of each face of the cube.
- Each Zn^{2+} ion is surrounded tetrahedrally by four S^{2-} ions and each S^{2-} ion is surrounded tetrahedrally by four Zn^{2+} ions. Thus, this structure has 4 : 4 coordination. (The ratio $r_{\text{Zn}^{2+}}/r_{\text{S}^{2-}} = 0.40$ which is greater than expected for exact fitting (0.225).)

Note: Zn^{2+} ions are present in alternate tetrahedral voids.

In an fcc unit cell, there are 8 TVs. Thus, there are four Zn^{2+} ions and 4 S^{2-} ions giving 4 ZnS units per unit cell.



Here electronegativity difference between Zn and S is very small (EN for Zn = 1.6 and EN for S = 2.5). Therefore, the bond between Zn and S has significant covalent character.

Figure 1.55(b) gives the structure of diamond and it is found that it is similar to that of ZnS (sphalerite).

A few examples of ionic compounds having ZnS structures are: CuCl, CuBr, CuI, AgI, and BeS.

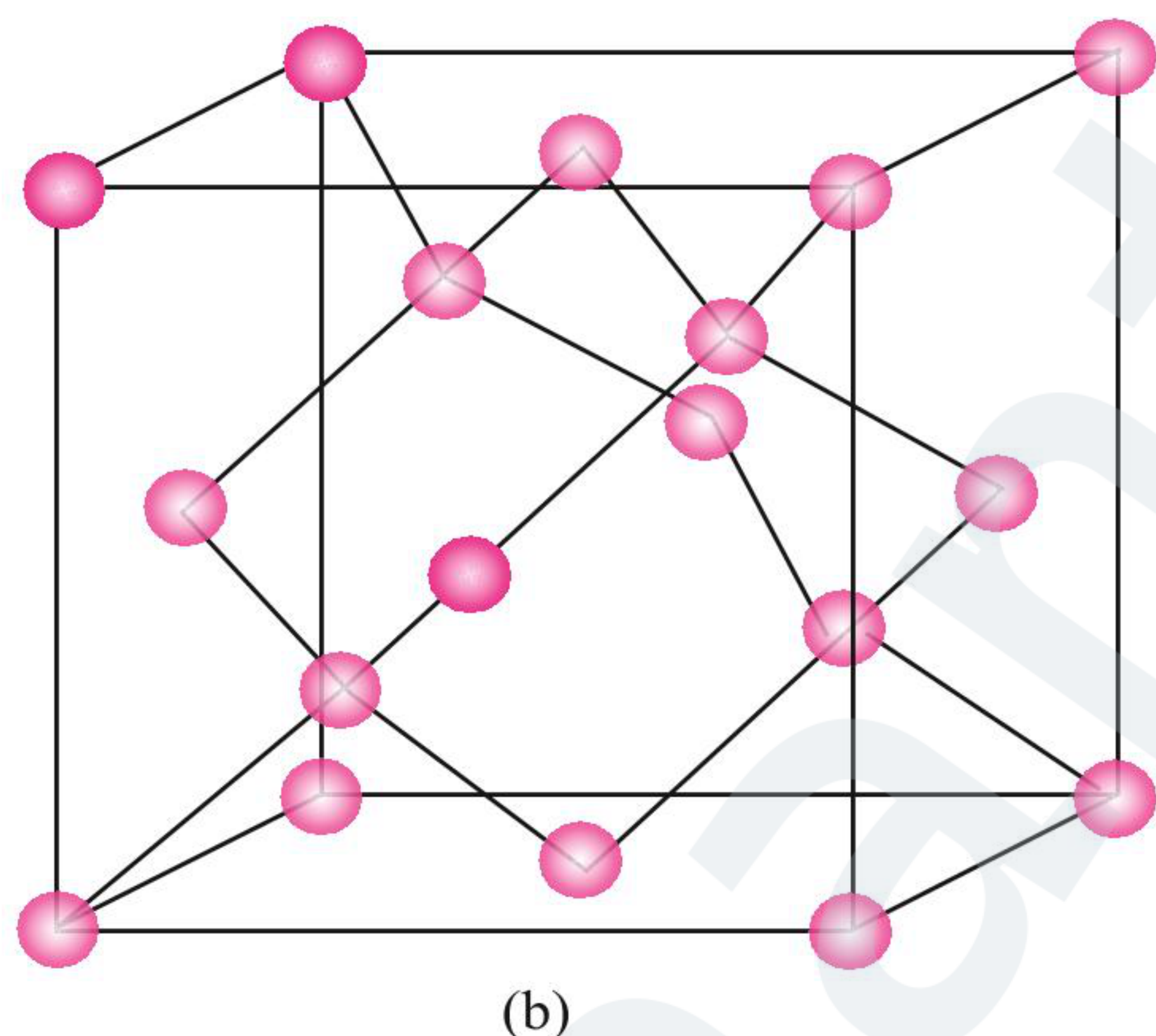


Fig. 1.55 (a) Structure of ZnS. (b) Diamond structure. Both structures (a) and (b) are identical

1.16.2 SIMPLE IONIC COMPOUNDS OF TYPE AB_2 (FLUORITE TYPE)

The next simplest type of ionic crystal structure is the 1 : 2 type popularly known as AB_2 -type structure. Calcium fluoride (fluorite), CaF_2 , is an example of AB_2 -type compounds (Fig. 1.56). Other ionic structures similar to CaF_2 structure are grouped under fluorite structure. The calcium ions, Ca^{2+} , are located at the face-centred cubic lattice points and, therefore, have cubic close-packed arrangement. The fluoride ions (F^- ions) occupy all the 8 tetrahedral voids. Thus, there are 4 Ca^{2+} ions and 8 F^- ions in the unit cell of calcium fluoride.

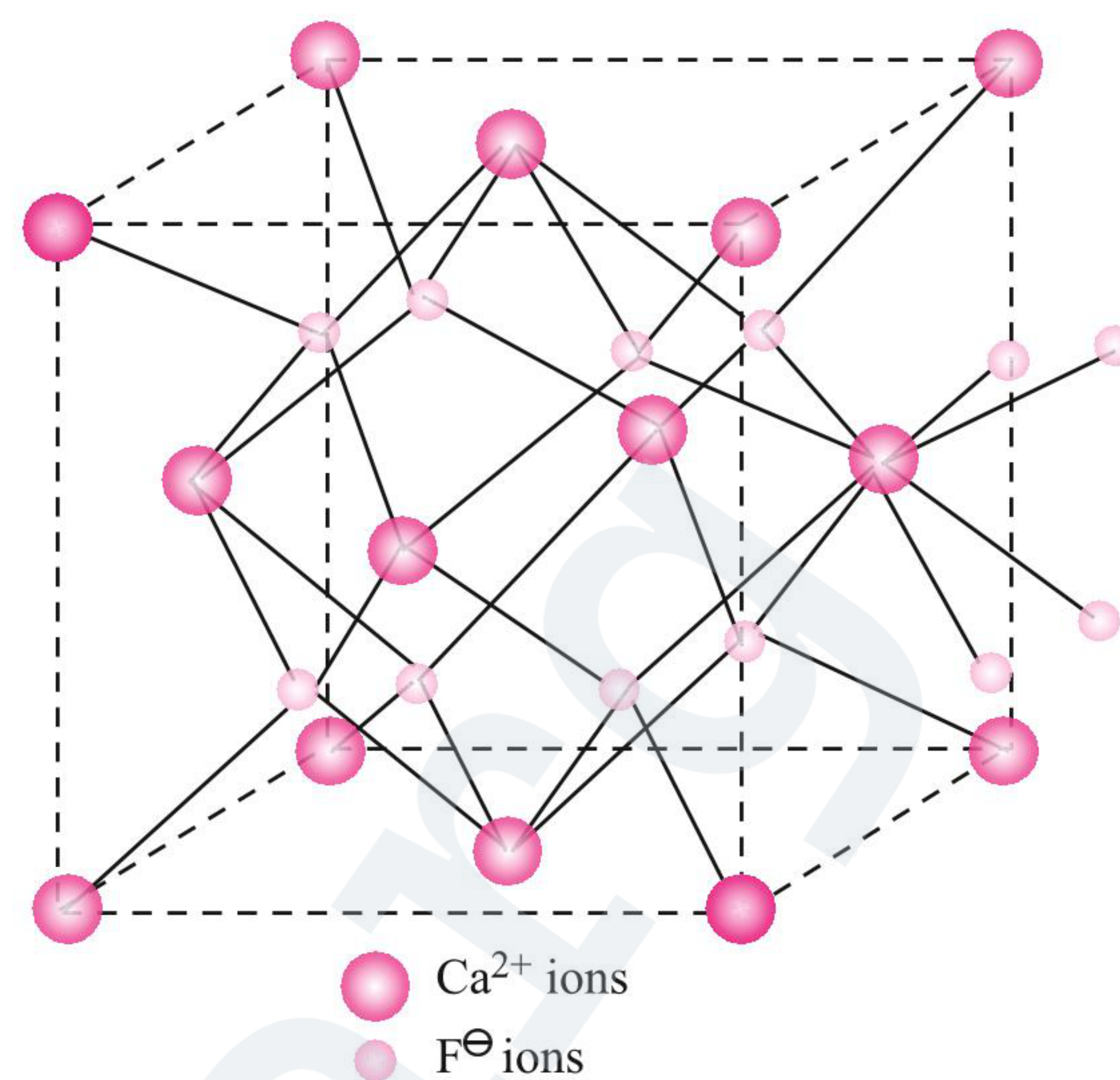


Fig. 1.56 Structure of CaF_2 (fluorite)

Note: Here negative ions (anions) (F^- ions) are present in all tetrahedral voids.

Coordinate number of AB_2 -type structure

Since each Ca^{+2} surrounded by = 8 F^- ions

Each F^- is surrounded by = 4 Ca^{+2} ions

Thus, the structure has 8 : 4 coordination. Other ionic compounds that have fluoride structure are SrF_2 , BaF_2 , PbF_2 , and BaCl_2 .

1.16.3 SIMPLE IONIC COMPOUNDS OF TYPE A_2B (ANTIFLUORITE TYPE)

Several A_2B -type or 2:1-type compounds have structures opposite to the fluorite structure; hence the so-called antifluorite structure. In an antifluorite structure the position of cations and anions as obtained in the fluorite structure gets reversed. In this structure, the smaller cations occupy the positions of fluoride ions in the fluorite structure and the larger anions occupy the positions of the calcium ions in the fluorite structure. For example, in Na_2O , oxide ions (O^{2-}) have a cubic close-packed arrangement and Na^+ ions occupy all the tetrahedral voids (Fig. 1.57). There are several oxides and sulphides which have antifluorite structure such as Li_2O , K_2O , Rb_2O , and Rb_2S .

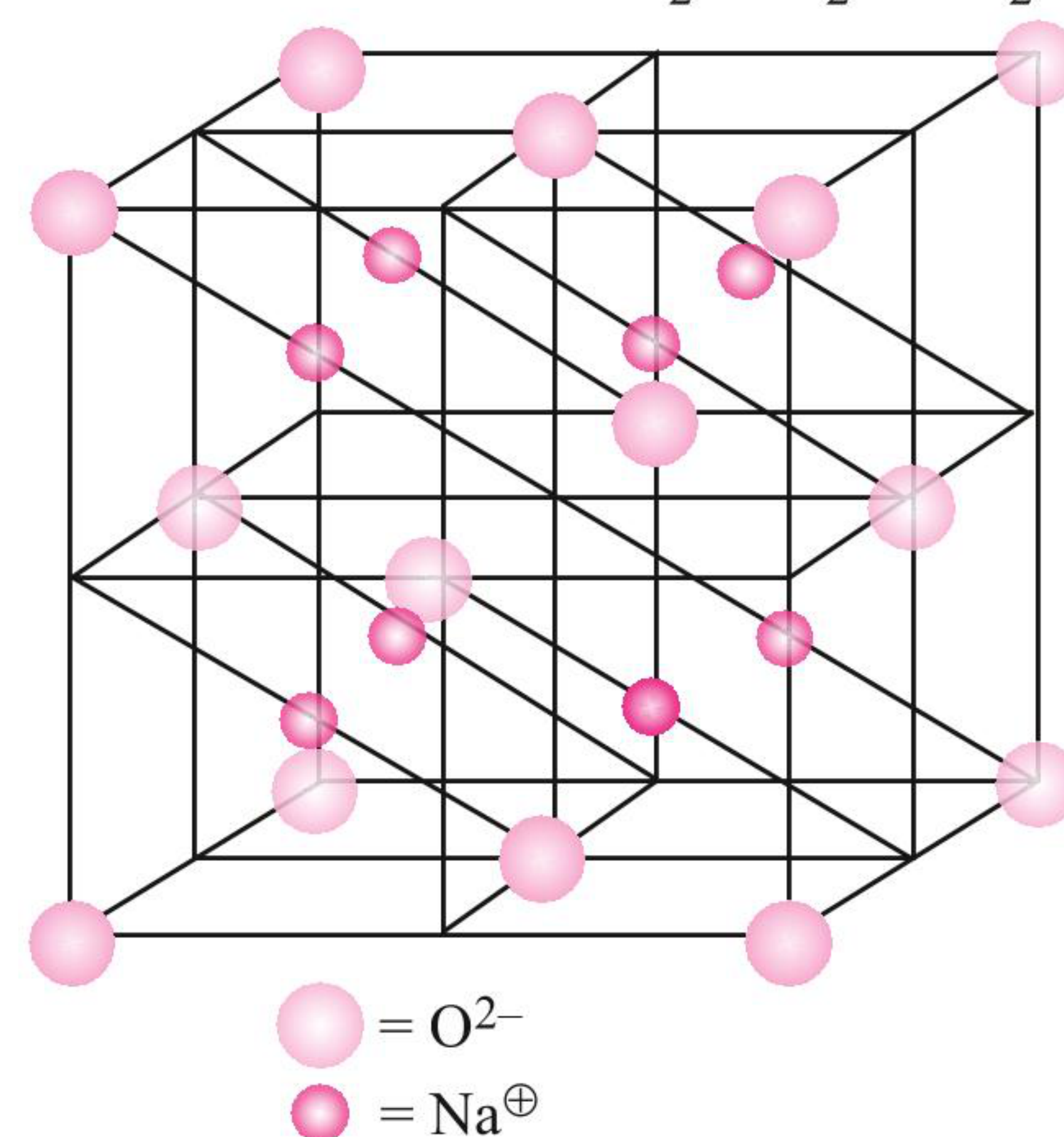


Fig. 1.57 Na_2O structure of antifluorite type

Coordination number of A_2B -type structure:

Each O^{2-} ions is surrounded by eight Na^+ ions.

Each Na^+ ion is surrounded by four O^{2-} .

Thus, the structure has 4 : 8 coordination.

1.16.4 RELATION BETWEEN EDGE LENGTH A AND RADIUS OF CATION AND ANION IN IONIC COMPOUNDS

a. For bcc-type (CsCl) structure

In CsCl lattice, anions (e.g., $\text{Cl}^\ominus$ ions) are at corners of the cube and cations (e.g., $\text{Cs}^\oplus$ ions) are at the body centre of the cube as shown in Fig. 1.58.

From the figure, it is clear that AD is the body diagonal of the cube.

$$\begin{aligned}\therefore (AD)^2 &= (AC)^2 + (DC)^2 \\ &= [(AB)^2 + (BC)^2] + (DC)^2 \\ (2r_\ominus + 2r_\oplus)^2 &= 3a^2 \\ \therefore (r_\oplus + r_\ominus) &= \frac{\sqrt{3}}{2}a\end{aligned}$$

b. For fcc-type (close-packed) structures (e.g., NaCl type)

In NaCl lattice, anions (i.e., $\text{Cl}^\ominus$ ions) are at the corners and face centre of the cube. Thus, Z_{eff} of $\text{Cl}^\ominus = 4$.

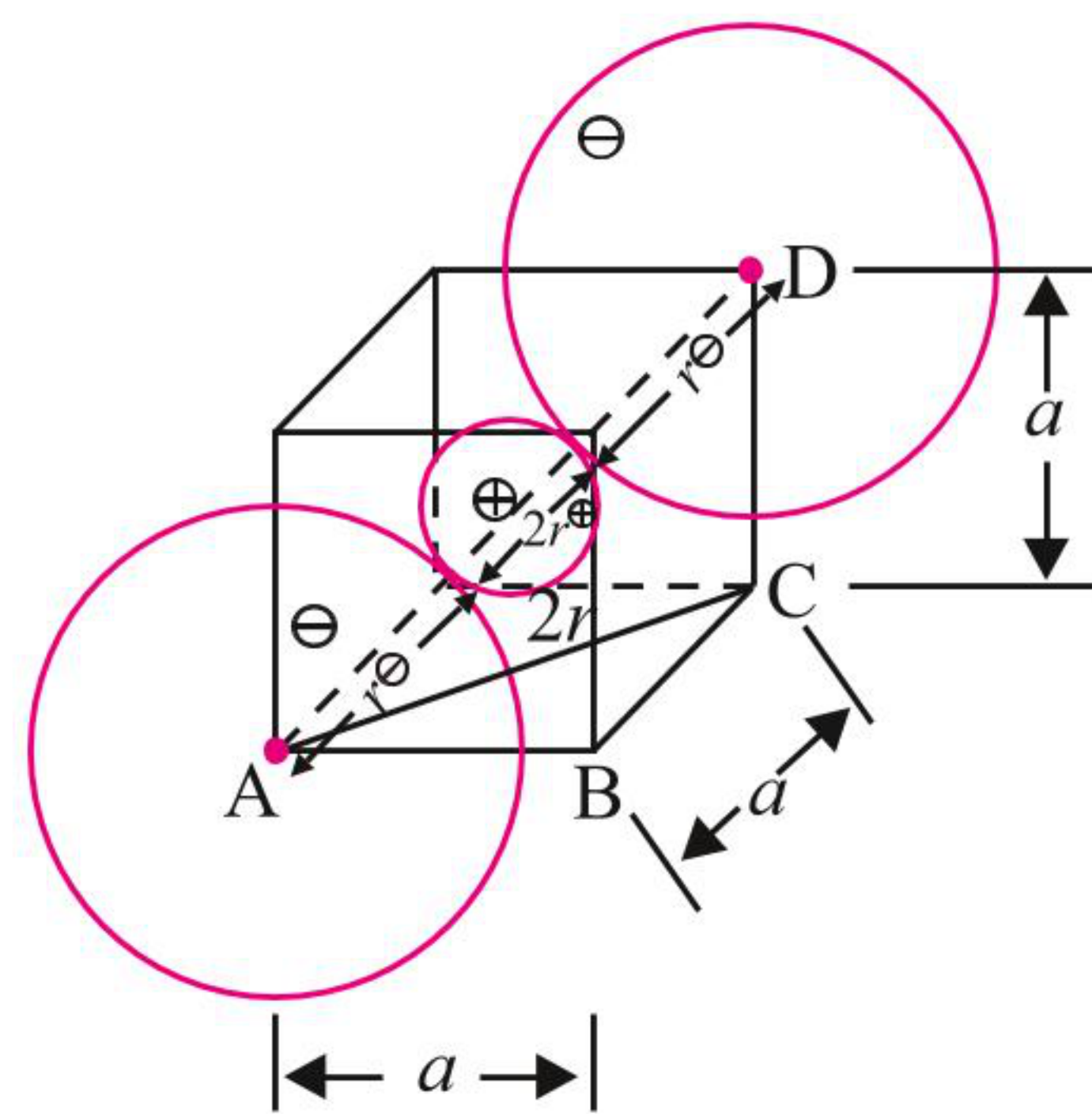


Fig. 1.58

Cations (i.e., $\text{Na}^\oplus$ ions) are in all octahedral voids formed at the edge centre and body centre of the cube as shown in Fig. 1.59:

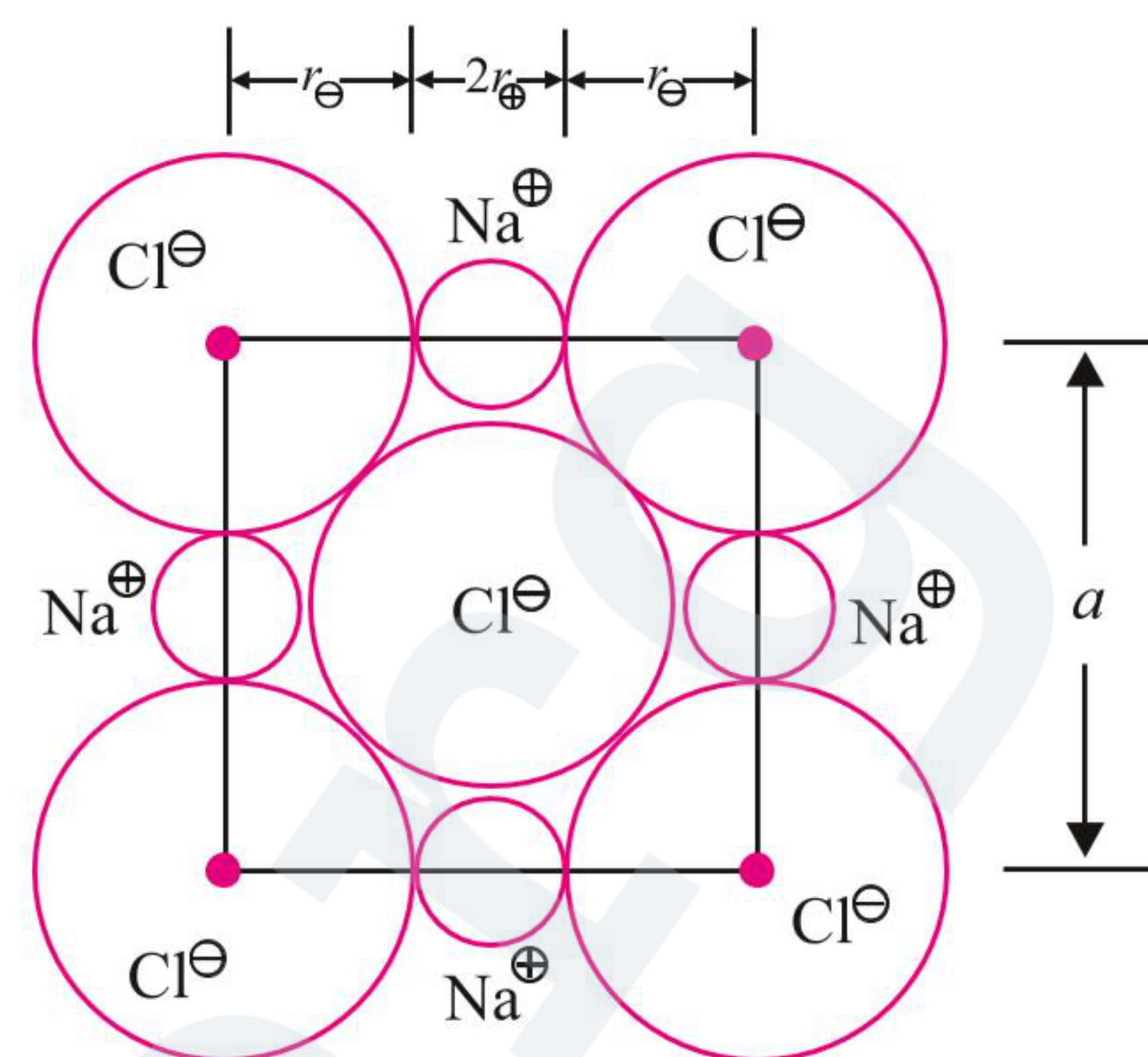


Fig. 1.59

From the figure, it is clear

$$\begin{aligned}(2r_\oplus + 2r_\ominus) &= a \\ \therefore (r_\oplus + r_\ominus) &= \frac{a}{2}\end{aligned}$$

Table 1.12 Summary of the main characteristics and examples of some simple ionic solids

Crystal structure	Brief description	Examples	Coordination number	Number of formula unit/units cell	Coordination number
Type AB: Rock salt (NaCl) type	It has fcc arrangement in which $\text{Cl}^\ominus$ ion occupy the corners and face centres of a cube while $\text{Na}^\oplus$ ions are present at the body and edge centres.	Halides of Li, Rb AgF, AgBr, NH_4Cl , NH_4Br , NH_4I	Each $\text{Na}^\oplus$ is surrounded by 6 $\text{Cl}^\ominus$. Each $\text{Cl}^\ominus$ is surrounded by 6 $\text{Na}^\oplus$ $\text{Na}^\oplus$ occupy all OVs. & all TV are empty.	General formula A_4B_4 or 4AB $Z_{\text{eff}} = 4$	6 : 6
Radius:	$(r_\oplus + r_\ominus) = a/2$				
Caesium chloride (CsCl) type	It has bcc arrangement with $\text{Cs}^\oplus$ at the body centre and $\text{Cl}^\ominus$ ions at the corners of a cube or vice versa.	CsCl, CsBr, CsI, CsCN, TlCl, TlBr TlI, and TlCN	Each $\text{Cs}^\oplus$ is surrounded by 8 $\text{Cl}^\ominus$. Each $\text{Cl}^\ominus$ is surrounded by 8 $\text{Cs}^\oplus$.	General formula AB $Z_{\text{eff}} = 1$	8 : 8
Radius for bcc type	$(r_\oplus + r_\ominus) = \frac{\sqrt{3}}{2}a$				
Zinc blende (ZnS) (sphalerite) type	It has ccp arrangement in which S^{2-} ions form fcc and each Zn^{2+} ion is surrounded tetrahedrally by S^{2-} ion and vice versa.	CuCl , CuBr , CuI , AgI 50% of TV are empty 100% of OV are empty	Each Zn^{2+} is surrounded by 4 S^{2-} . Each S^{2-} is surrounded by 4 Zn^{2+} . Zn^{2+} are in alternate TVs.	General formula A_4B_4 or 4AB $Z_{\text{eff}} = 4$	4 : 4
Type AB₂ Fluorite (CaF_2) type	It has ccp arrangement in which Ca^{2+} ions form fcc with each Ca^{2+} ion surrounded by 8 $\text{F}^\ominus$ ions and each $\text{F}^\ominus$ ion by 4 Ca^{2+} ions	BaF_2 , BaCl_2 , SrF_2 , SrCl_2 , CdF_2 , PbF_2	Each Ca^{2+} is surrounded by 8 $\text{F}^\ominus$. Each $\text{F}^\ominus$ is surrounded by 4 Ca^{2+} . $\text{F}^\ominus$ ions occupy all the 8 TVs.	General formula A_4B_8 or AB_2 $Z_{\text{eff}} = 4$ 100% TV occupied 100% OV empty.	8 : 4

Type A_2B Anti-fluorite type	Here O^{2-} ions form the ccp arrangement so that each Na^+ ion is surrounded by 4 O^{2-} ions and each O^{2-} ion is surrounded by 8 Na^+ ions.	Na_2O, Li_2O	Each Na^+ is surrounded by 4 O^{2-} . Each O^{2-} is surrounded by 8 Na^+ . Na^+ ions occupy all the TVs.	General formula A_8B_4 or A_2B $Z_{eff} = 4$	4 : 8
---	--	----------------	---	--	-------

1.17 STRUCTURE OF DIAMOND

Solids which follow the structure of diamond are called “diamond cubic” [Fig. 1.55(b)]. Diamond has fcc structure with four more atoms that are found to be present in the alternate tetrahedral voids.

So, Z_{eff} of C-atoms in diamond cubic

= Z_{eff} in fcc unit cell + Z_{eff} in alternate TVs

$$= \underbrace{\left[\frac{1}{8} \times 8 + \frac{1}{2} \times 6 \right]}_{\text{fcc unit cell}} + \underbrace{[1 \times 4]}_{\text{Alternate TVs}} = 8$$

The C-atom in TVs touches its four surrounding atoms (nearest neighbours), so the coordination number = 4.

The carbon atoms in an fcc lattice do not touch atoms at all. But C-atoms which are present in tetrahedral voids touch the surrounding four atoms. So, the centre-to-centre distance between two C-atoms is:

$$2r = \frac{\sqrt{3}}{4}a \Rightarrow r = \frac{\sqrt{3}}{8}a.$$

where a is the length of the unit cell and r is the radius of C-atom.

Packing efficiency (PE) of diamond cubic (dc)

$$PE = \frac{Z_{eff} \times \text{Volume of C-atom}}{a^3} \times 100$$

$$= \frac{8 \times \frac{4}{3} \pi r^3 \times 100}{a^3} \quad \left(r = \frac{\sqrt{3}a}{8} \right)$$

$$= \frac{8 \times \frac{4}{3} \pi \left(\frac{\sqrt{3}}{8} \right)^3 \cancel{a^3} \times 100}{\cancel{a^3}}$$

$$= \frac{32}{3} \pi \left(\frac{\sqrt{3}}{8} \right)^3 \times 100 = 34\%$$

Germanium, silicon, and grey tin also crystallize in the same way as diamond does.

1.18 SPINEL STRUCTURES

Spinel structures are examples of an ionic crystal with more than two types of ions. Spinel is a compound with two different cations A^{2+} and B^{3+} and oxide (O^{2-}) as the anion, with the general formula $A^{+2}B_2^{+3}O_4^{-2}$.

Note: Many substances of the type ($A^{4+}B_2^{2+}O_4^{2-}$) also have spinel-type structure.

1.18.1 NORMAL SPINEL STRUCTURES

In such structures, O^{2-} anions form the fcc packing and 1/8th of TVs are occupied by divalent metal ion A^{2+} and half of the

octahedral voids are occupied by trivalent metal ions (B^{3+}). In the unit cell, we have

Z_{eff} of O^{2-} anion in fcc packing = 4/unit cell

Number of TVs = 8/unit cell

Number of OVs = 4/unit cell

Therefore,

$$\text{Number of } A^{2+} \text{ ions} = \frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 8 = 1$$

$$\text{Number of } B^{3+} \text{ ions} = \frac{1}{2} \times \text{OVs} = \frac{1}{2} \times 4 = 2$$

$$\text{General formula} = A_1^{2+} B_2^{3+} O_4^{2-} \equiv AB_2O_4$$

Examples: $ZnAl_2O_4$, $MgAl_2O_4$, $ZnFe_2O_4$.

Alternatively

Let Z_{eff} of O^{2-} anion in fcc packing = 1/atom

Number of TVs = 2/atom

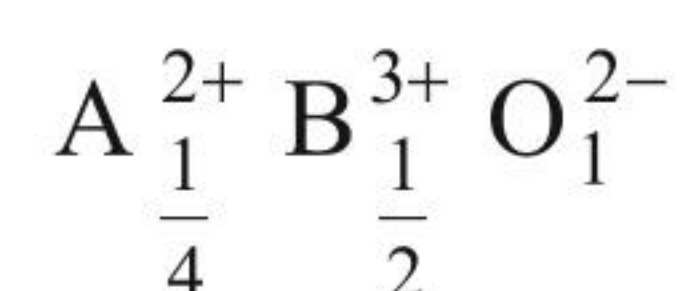
Number of OVs = 1/atom

Therefore,

$$\text{Number of } A^{2+} \text{ ions} = \frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 2 = \frac{1}{4}$$

$$\text{Number of } B^{3+} \text{ ions} = \frac{1}{2} \times \text{OVs} = \frac{1}{2} \times 1 = \frac{1}{2}$$

General formula:



On simplifying, we get the formula AB_2O_4 .

a. Ratio of TV/OV occupied in spinel structure

Number of TV occupied = 1

Number of OVs occupied = 2

$$\text{Ratio} \left(\frac{\text{TV}}{\text{OV}} \right)_{\text{occupied}} = \frac{1}{2} = 1:2$$

b. Ratio of TV/OV unoccupied in spinel structure

Number of TVs unoccupied = $8 - 1 = 7$

Number of OVs unoccupied = $4 - 2 = 2$

$$\text{Ratio} \left(\frac{\text{TV}}{\text{OV}} \right)_{\text{unoccupied}} = \frac{7}{2} = 7:2$$

1.18.2 INVERSE SPINEL STRUCTURES

In such structures, O^{2-} anions form the fcc packing and 1/8th of the tetrahedral voids are occupied by divalent metal ion A^{2+} . Trivalent metal ions B^{3+} are present in $\left(\frac{1}{8} \text{th TV} + \frac{1}{4} \text{th OV} \right)$.

Thus, in the unit cell, we have

Z_{eff} of O^{2-} anion in fcc packing = 4/unit cell

Number of TVs = 8/unit cell

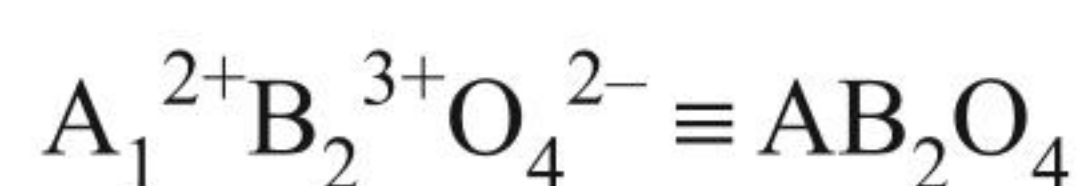
Number of OVs = 4/unit cell

Therefore,

$$\text{Number of } A^{2+} \text{ ions} = \frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 8 = 1$$

$$\begin{aligned} \text{Number of } B^{3+} \text{ ions} &= \frac{1}{8} \times \text{TVs} + \frac{1}{4} \times \text{OVs} \\ &= \frac{1}{8} \times 8 + \frac{1}{4} \times 4 \\ &= 1 + 1 = 2 \end{aligned}$$

General formula:



Alternatively

Let Z_{eff} of O^{2-} anion in fcc packing = 1/atom

Number of TVs = 2/atom

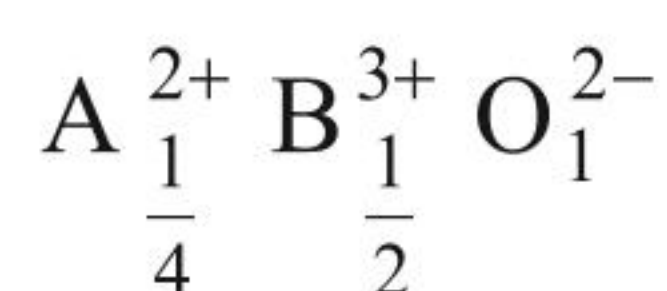
Number of OVs = 1/atom

Therefore,

$$\text{Number of } A^{2+} \text{ ions} = \frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 2 = \frac{1}{4}$$

$$\begin{aligned} \text{Number of } B^{3+} \text{ ions} &= \frac{1}{8} \times \text{TVs} + \frac{1}{4} \times \text{OVs} \\ &= \frac{1}{8} \times 2 + \frac{1}{4} \times 1 \\ &= \frac{1}{4} + \frac{1}{4} \\ &= \frac{2}{4} = \frac{1}{2} \end{aligned}$$

So, general formula:



Simplifying, formula = AB_2O_4 .

a. Ratio of TV/OV occupied in inverse spinel structure

Number of TV occupied = 1 + 1 = 2

Number of OV occupied = 1

$$\text{So, ratio } \left(\frac{\text{TV}}{\text{OV}} \right)_{\text{occupied}} = \frac{2}{1} = 2:1$$

This ratio $\left(\frac{\text{TV}}{\text{OV}} \right)_{\text{occupied}}$ in inverse spinel structure is

reverse to that of the spinel structure. Hence, this is called inverse spinel structure.

b. Ratio of TV/OV unoccupied in inverse spinel structure

Number of TVs unoccupied = 8 - 2 = 6

Number of OVs unoccupied = 4 - 1 = 3

$$\text{So, ratio } \left(\frac{\text{TV}}{\text{OV}} \right)_{\text{unoccupied}} = \frac{6}{3} = 2:1$$

1.19 CORUNDUM STRUCTURE

In this structure, O^{2-} anions form hcp and cations A^{3+} are present in two-thirds of the octahedral voids. The general formula of a compound is A_2O_3 . Examples are Fe_2O_3 , Al_2O_3 , Cr_2O_3 .

Calculation of general formula

First method:

Z_{eff} of O^{2-} in hcp packing = 6/unit cell

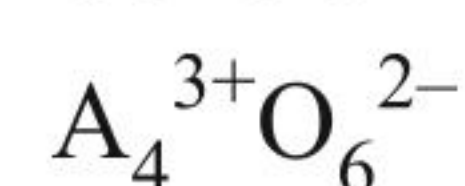
Number of TVs = 12/unit cell

Number of OVs = 6/unit cell

Therefore,

$$\text{Number of } A^{3+} = \frac{2}{3} \times \text{OVs} = \frac{2}{3} \times 6 = 4$$

General formula:



Simplifying, formula is A_2O_3 .

Second method:

Let Z_{eff} of O^{2-} = 1/atom

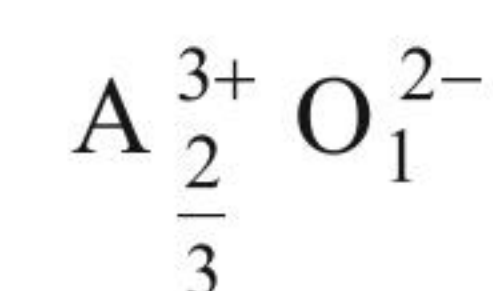
Number of TVs = 2/atom

Number of OVs = 1/atom

Therefore,

$$\text{Number of } A^{3+} = \frac{2}{3} \times \text{OVs} = \frac{2}{3} \times 1 = \frac{2}{3}$$

General formula:



Simplifying, formula is A_2O_3 .

Coordination number of corundum

From the formula, the ligancy of ($A^{3+} : O^{2-}$) in A_2O_3 is 6 : 4.

Note: Ligancy of A^{3+} = Number of O^{2-} ions
Ligancy of O^{2-} = Number of A^{3+} ions

1.19.1 STRUCTURE OF THE OXIDES OF IRON

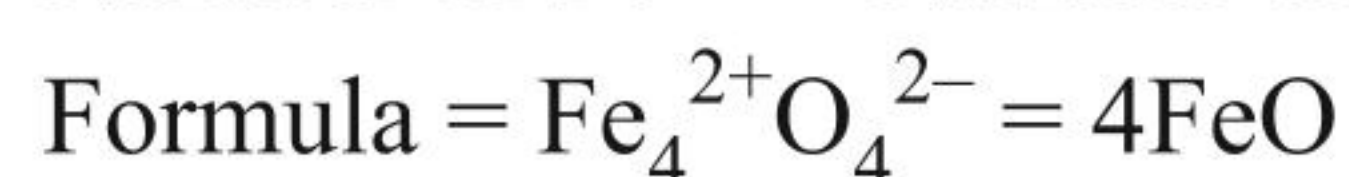
Iron forms three important oxides which are FeO , Fe_2O_3 , and Fe_3O_4 . These compounds have non-stoichiometric composition and are easily oxidized or reduced into each other. These aspects are explained on the basis of their crystal structure as follows:

a. Structure of FeO : If the oxide ions (O^{2-}) form a cubic close packing with all the octahedral voids occupied by Fe^{2+} ions, we will get a perfect rock salt ($NaCl$) lattice. The formula of the oxide then would be FeO . However, actually the oxide is found to be non-stoichiometric with the composition $Fe_{0.95}O$ (called wustite). This structure can be explained by assuming that a small number of Fe^{2+} ions in these octahedral voids are replaced by Fe^{3+} ions (of course every three Fe^{2+} ions would be replaced by two Fe^{3+} ions to maintain electrical neutrality). Consequently, we get Fe-deficient crystals.

Formula

Number of O^{2-} in ccp = 4/unit cell

Number of Fe^{2+} = Number of OVs = 4/unit cell



b. Structure of red brown $\alpha\text{-Fe}_2\text{O}_3$

It is an hcp lattice of O^{2-} ions with Fe^{3+} ions in two-thirds of the octahedral voids.

Formula

Number of O^{2-} in hcp = 6/unit cell

Number of OVs = 6/unit cell

$$\begin{aligned}\text{Number of } \text{Fe}^{3+} \text{ ions} &= \frac{2}{3} \times \text{OVs} \\ &= \frac{2}{3} \times 6 = 4/\text{unit cell}\end{aligned}$$

$$\text{Formula} = \text{Fe}_4^{3+}\text{O}_6^{2-}$$

Simplifying: Fe_2O_3 .

Alternatively

If all Fe^{2+} ions in FeO is replaced by Fe^{3+} ions, then as every three Fe^{2+} ions can be replaced by two Fe^{3+} ions to maintain electrical neutrality, the ratio between Fe^{3+} and O^{2-} will now be 2 : 3 and not 1 : 1, we get the oxide Fe_2O_3 .

c. Structure of $\gamma\text{-Fe}_2\text{O}_3$: If $\alpha\text{-Fe}_2\text{O}_3$ is oxidized, $\gamma\text{-Fe}_2\text{O}_3$ is formed which has a ccp lattice of O^{2-} ions with Fe^{3+} ions randomly distributed in both octahedral and tetrahedral voids.

d. Structure of Fe_3O_4 : Fe_3O_4 (magnetite) is formed as a black solid by igniting Fe_2O_3 at 1400°C . Fe_3O_4 is a mixed oxide $\text{Fe}^{\text{II}}\text{O} \cdot \text{Fe}_2^{\text{III}}\text{O}_3$ or $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$ which has an inverse spinel structure.

It is a ccp lattice of O^{2-} with larger Fe^{2+} in 1/8th of tetrahedral voids. Fe^{3+} ions are present in 1/4th of octahedral voids and 1/8th of tetrahedral voids.

Formula

Number of O^{2-} in ccp lattice = 4/unit cell

Number of TVs and OVs, respectively, are 8 and 4 per unit cell.

$$\text{Number of } \text{Fe}^{2+} \text{ ions} = \frac{1}{8} \times \text{TVs} = \frac{1}{8} \times 8 = 1$$

$$\begin{aligned}\text{Number of } \text{Fe}^{3+} \text{ ions} &= \frac{1}{8} \times \text{TVs} + \frac{1}{4} \times \text{OVs} \\ &= \frac{1}{8} \times 8 + \frac{1}{4} \times 4 \\ &= 1 + 1 = 2\end{aligned}$$

$$\therefore \text{General formula} = \text{Fe}_1^{2+}\text{Fe}_2^{3+}\text{O}_4^{2-} \equiv \text{Fe}_3\text{O}_4$$

All these compounds are called *ferrites*, but they are now represented as mixed oxides.

e. Another example of the iron oxide structure is MgFe_2O_4 , where Mg^{2+} ions replace Fe^{2+} ions of Fe_3O_4 . In the so-called normal spinel structure of compounds of the general formula AB_2O_4 (e.g., MgAl_2O_4 and ferrites such as ZnFe_2O_4), the divalent cations (Mg^{2+} , Fe^{2+}) are in tetrahedral voids and

the trivalent B^{3+} ions (Fe^{3+} , Al^{3+}) are in octahedral voids. Many of the ferrites which possess spinel-type structure are important magnetic materials used in telephone or memory loops in computer. Fe_3O_4 (magnetic) is the load stone used by ancient travellers to find the direction.

ILLUSTRATION 1.25

In a compound, oxide ions are arranged in ccp. One-sixth of the tetrahedral voids are occupied by cations (A) and one-third of OVs are occupied by cations (B). **(a)** What is the formula of the compound? **(b)** What are the charges on A and B?

Sol. a. First method

Number of O^{2-} ions in ccp = 4

Number of TVs = 8

Number of OVs = 4

$$\begin{aligned}\text{Number of cations A} &= \frac{1}{6} \times \text{TVs} \\ &= \frac{1}{6} \times 8 = \frac{4}{3}\end{aligned}$$

$$\begin{aligned}\text{Number of cations B} &= \frac{1}{3} \times \text{OVs} \\ &= \frac{1}{3} \times 4 = \frac{4}{3}\end{aligned}$$

$$\text{Formula } \text{A}_{\frac{4}{3}}\text{B}_{\frac{4}{3}}\text{O}_4^{2-} \equiv \text{ABO}_3$$

Second method

Let the number of O^{2-} in ccp = 1/atom

Number of TVs = 2/atom.

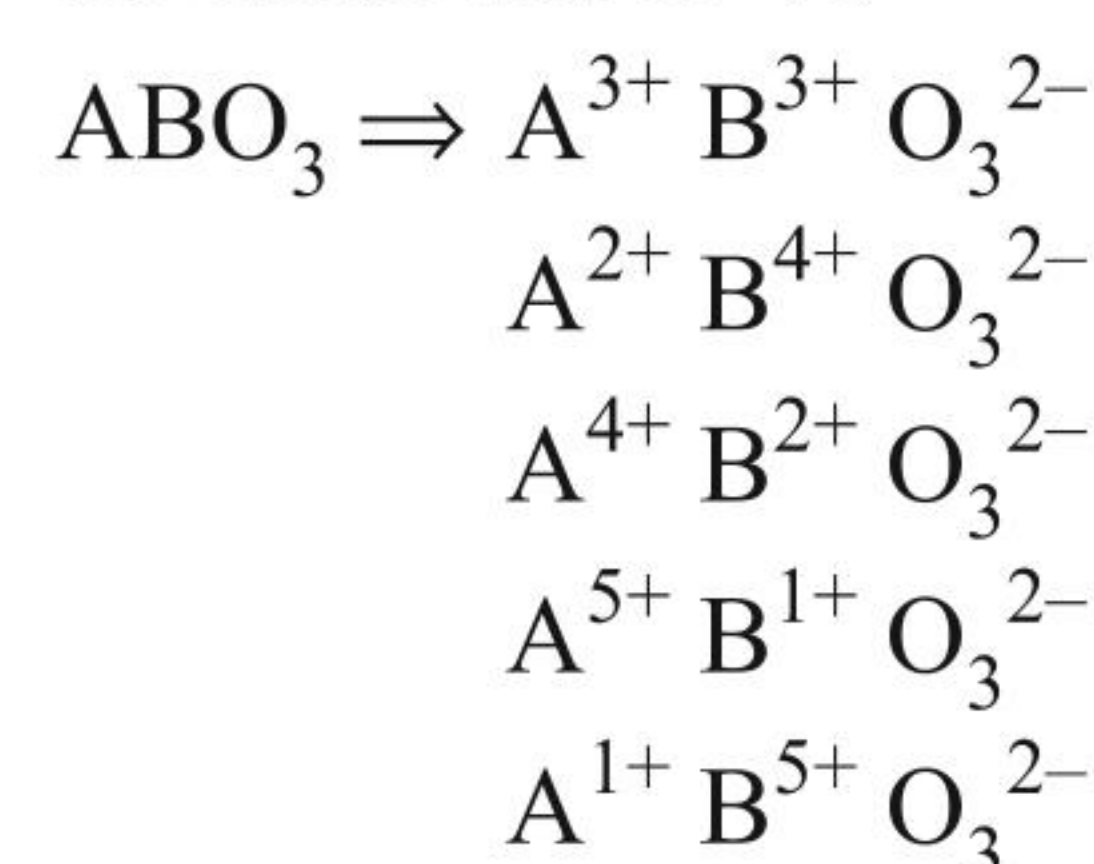
Number of OVs = 1/atom.

$$\text{Number of cations A} = \frac{1}{6} \times \text{TV} = \frac{1}{6} \times 2 = \frac{1}{3}$$

$$\text{Number of cations B} = \frac{1}{3} \times \text{OV} = \frac{1}{3} \times 1 = \frac{1}{3}$$

$$\text{Thus, formula is: } \text{A}_{1/3}\text{B}_{1/3}\text{O}_1^{2-} \Rightarrow \text{ABO}_3$$

b. Various possibilities of charge on A and B since charge on oxide ion is -2 .

**ILLUSTRATION 1.26**

A compound is made of two elements P and Q. Atoms Q are in ccp arrangement while atoms P occupy all the tetrahedral voids. What is the formula of the compound?

Sol. First method

Number of Q atoms in ccp = 4/unit cell

Number of TVs = 8/unit cell

Number of OVs = 4/unit cell

Number of P atoms = Number of TVs = 8

Thus formula = $P_8Q_4 \Rightarrow P_2Q$.

Second method

Let number of Q atoms in ccp = 1/atom

Number of TVs = 2/atom

Number of OVs = 1/atom

Number of P atoms = Number of TVs = 2

Thus, formula = P_2Q

ILLUSTRATION 1.27

Two ions $A^{\oplus}$ and $B^{\ominus}$ have radii 88 and 200 pm, respectively. In the close-packed crystal of compound AB, predict coordination number of $A^{\oplus}$.

Sol. $\frac{r_{\oplus}}{r_{\ominus}} = \frac{r(A^{\oplus})}{r(B^{\ominus})} = \frac{88}{200} = 0.44$

It lies in the range 0.414 to 0.732.

Hence, the coordination number of $A^{\oplus} = 6$.

ILLUSTRATION 1.28

If the close-packed cations in an AB-type solid have a radius of 75 pm, what would be the maximum and minimum sizes of the anions filling the voids?

Sol. For close-packed AB-type solid,

$$\frac{r_{\oplus}}{r_{\ominus}} = 0.414 - 0.732$$

$$\begin{aligned} \therefore \text{Minimum value of } r_{\ominus} &= \frac{r_{\oplus}}{0.732} \\ &= \frac{75}{0.732} \text{ pm} = 102.5 \text{ pm} \end{aligned}$$

$$\text{Maximum value of } r_{\ominus} = \frac{r_{\oplus}}{0.414} = \frac{75}{0.414} = 181.2 \text{ pm}$$

ILLUSTRATION 1.29

If the radii of Mg^{2+} , $Cs^{\oplus}$, O^{2-} , S^{2-} , and $Cl^{\ominus}$ ions are 0.65, 1.69, 1.40, 1.84, and 1.81 Å, respectively, calculate the coordination number of the cations in the crystals of MgS, MgO, and CsCl.

Sol. CN of MgS

a. $\frac{Mg^{2+}}{S^{2-}} = \frac{0.65}{1.84} = 0.35$
(Range lies between 0.225 and 0.414)
 $\therefore \text{CN} = 4$

b. In MgO: $\frac{Mg^{2+}}{O^{2-}} = \frac{0.65}{1.40} = 0.48$
(Range lies between 0.414 and 0.732)
 $\therefore \text{CN} = 6$

c. In CsCl: $\frac{Cs^{\oplus}}{Cl^{\ominus}} = \frac{1.69}{1.81} = 0.93$
(Range lies between 0.732 and 1)
 $\therefore \text{CN} = 8$

1.20 PEROVSKITE STRUCTURE

The perovskite structure is a cubic lattice, with Ba^{2+} ions occupying the corners of the unit cell, O^{2-} ions occupying the face centres, and Ti^{4+} ions occupying the centres of the unit cell (Fig 1.60). Thus, the formula is:

$$\text{Number of } Ba^{2+} \text{ ions} = \frac{1}{8} \times 8 \text{ corners} = 1$$

$$\text{Number of } Ti^{4+} \text{ ions} = 1 \text{ body centre atom.}$$

$$\text{Number of } O^{2-} \text{ ions} = 6 \text{ faces} \times \frac{1}{2} \text{ face centre share} = 3$$

$$\text{Therefore, the formula is: } Ba^{2+}Ti^{4+}O_3^{2-} \equiv BaTiO_3$$

- a. Ti^{4+} ions are present at the body centre of the unit cell, therefore they are present in octahedral voids.

Thus, OVs at the centres of the unit cell constitute one-fourth of all the octahedral voids in an fcc lattice.

[Since total OV = 4(1 at body centre + 12/4 at edge centres)]

- b. Ti^{4+} ions at the centre of a unit cell has six nearest neighbour O^{2-} ions.
- c. The other octahedral voids located at the centres of the edges of unit cell have six nearest neighbours each as the case with any octahedral voids
But two out of the six neighbours are Ba^{2+} ions and four are O^{2-} ions.
- d. The proximity of two cations, Ba^{2+} and Ti^{4+} would be electrostatically unfavourable.

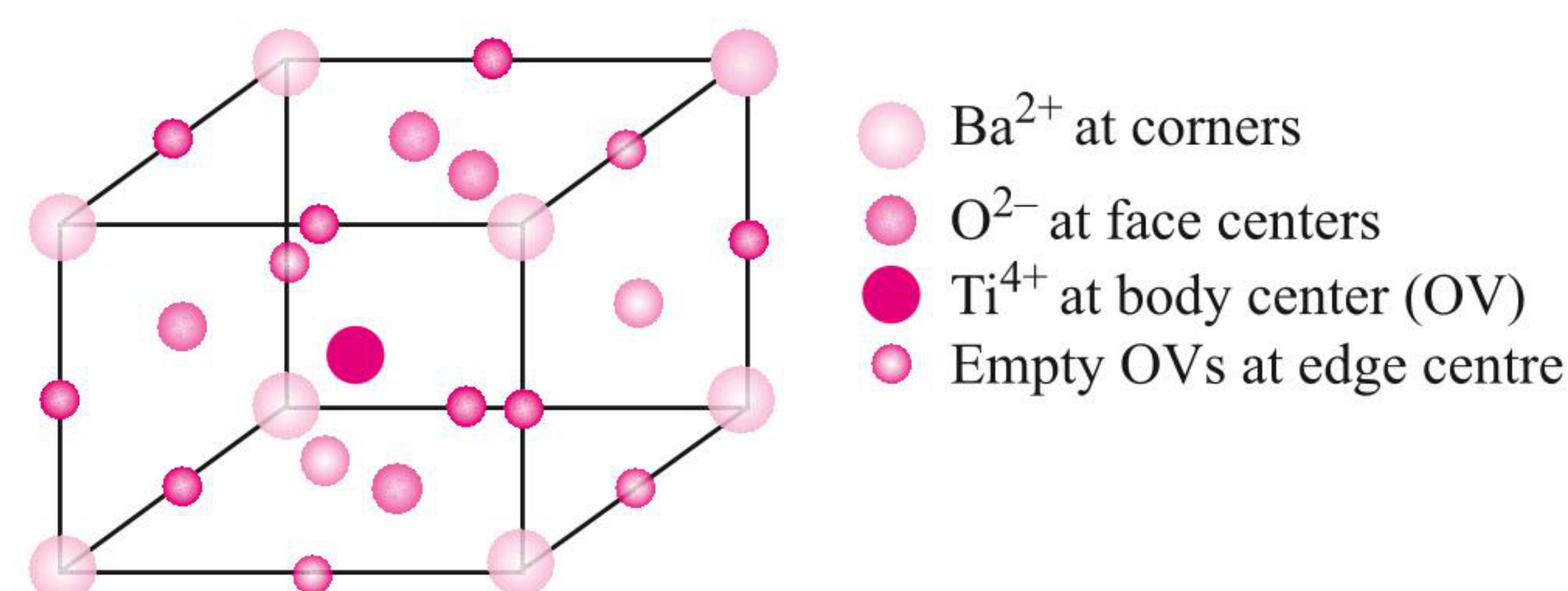


Fig. 1.60 Structure of perovskite

1.21 RUTILE STRUCTURE

TiO_2 exists in three forms called *anatase*, *brookite*, and *rutile*. The rutile structure is found in many crystals where the radius ratio is between 0.41 and 0.73.

It is not exactly a close-packed structure. Ti^{4+} ions in rutile are considered as forming a sufficiently distorted body centred cubic lattice (Fig. 1.61).

In rutile each Ti^{4+} ion is octahedrally surrounded by six O^{2-} ions whereas each O^{2-} is surrounded by only three Ti^{4+} ions arranged at the three corners of a plane triangle. The coordination numbers of Ti^{4+} and O^{2-} ions are 6 and 3, respectively.

$$\therefore \text{Formula is: } Ti_3^{4+}O_6^{2-} \text{ or } 2TiO_2.$$

Note: CN of cation = Number of anions
CN of anions = Number of cations

There are only a few cases where the radius ratio is below 0.41; examples are SiO_2 and BeF_2 . The coordination number of

Si^{4+} and Be^{2+} is 4 and that of O^{2-} and $\text{F}^{\ominus}$ is 2. However, these are appreciably covalent.

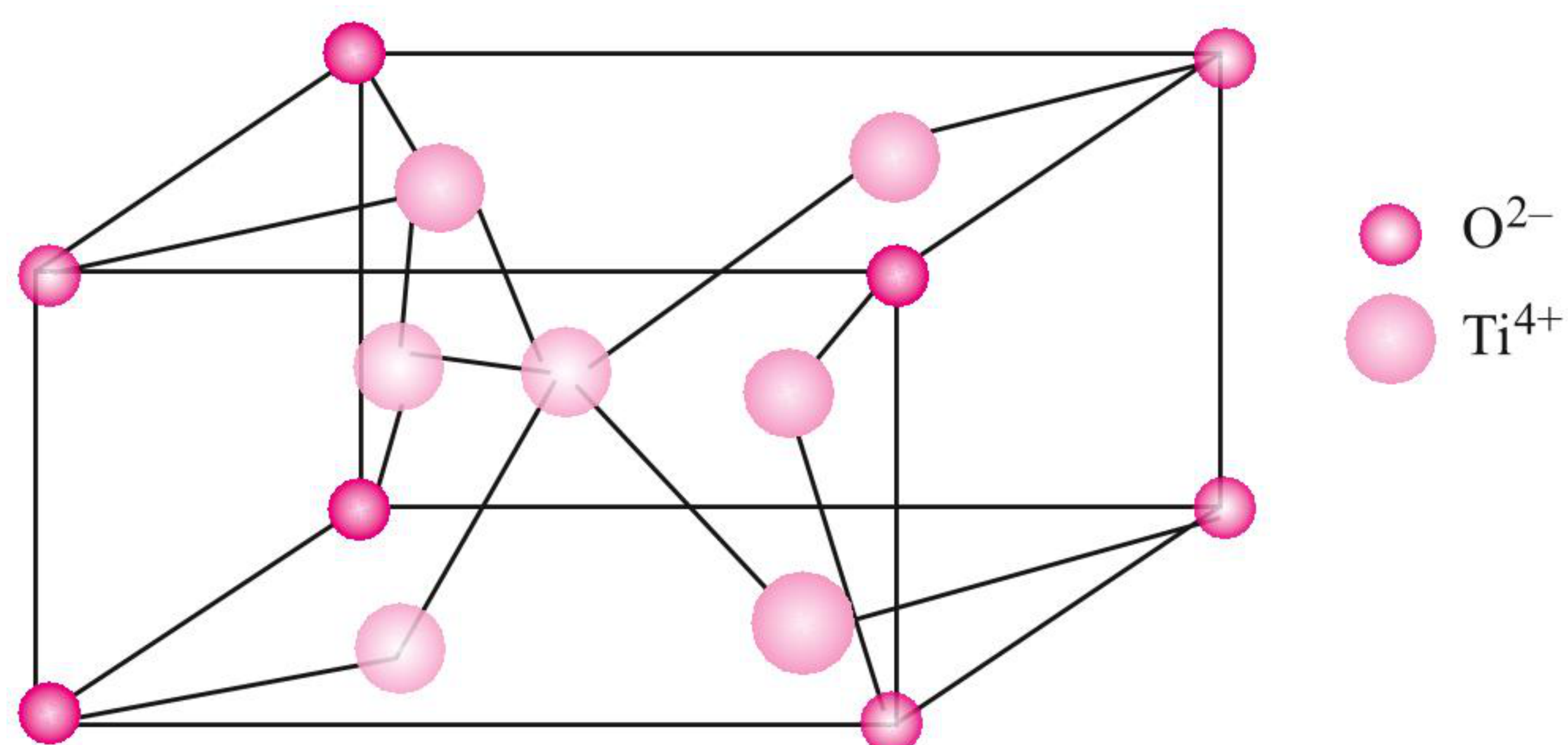
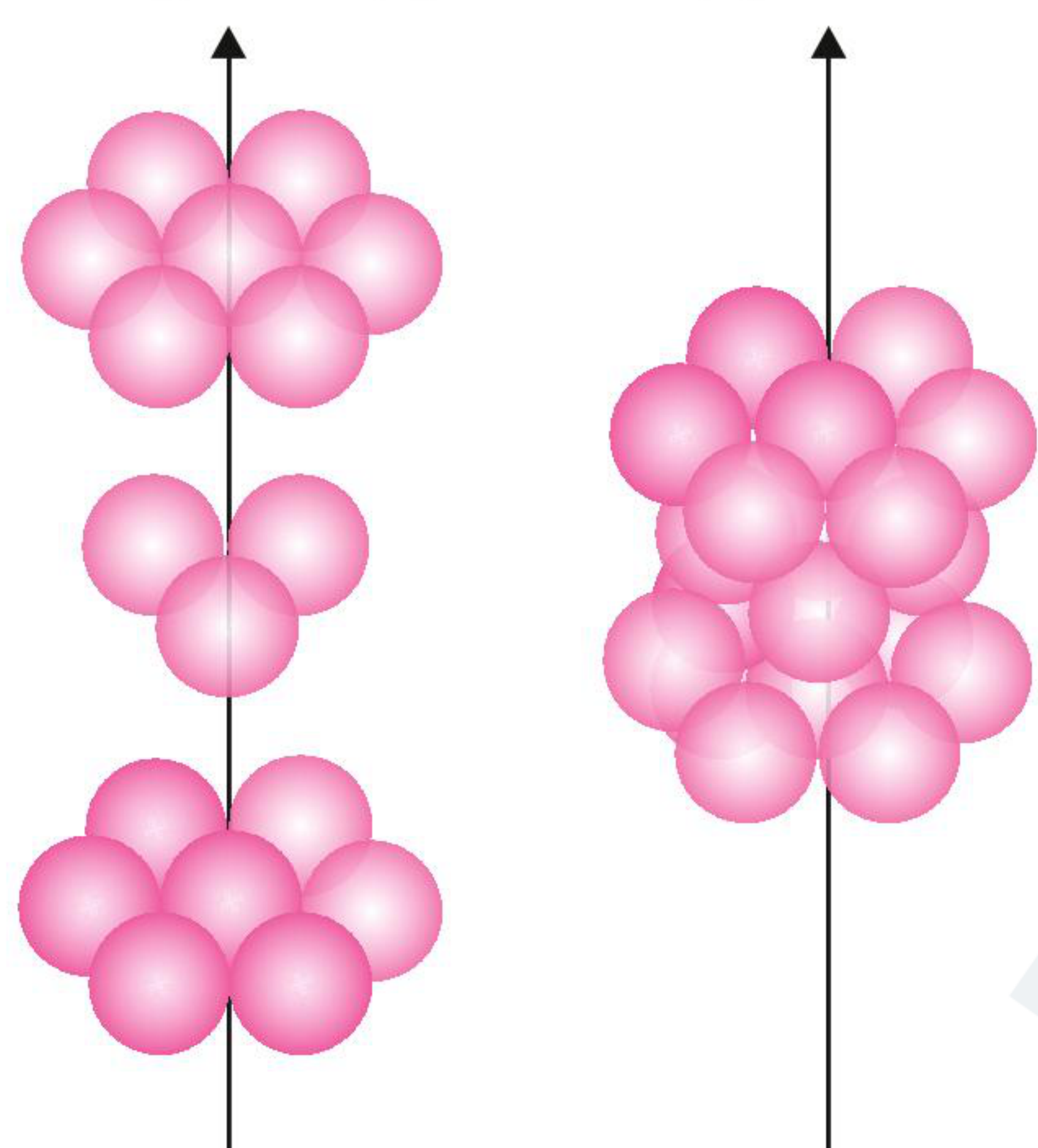


Fig. 1.61 Structure of rutile

1.22 CALCULATION OF EFFECTIVE ATOMS IN AN hcp UNIT CELL

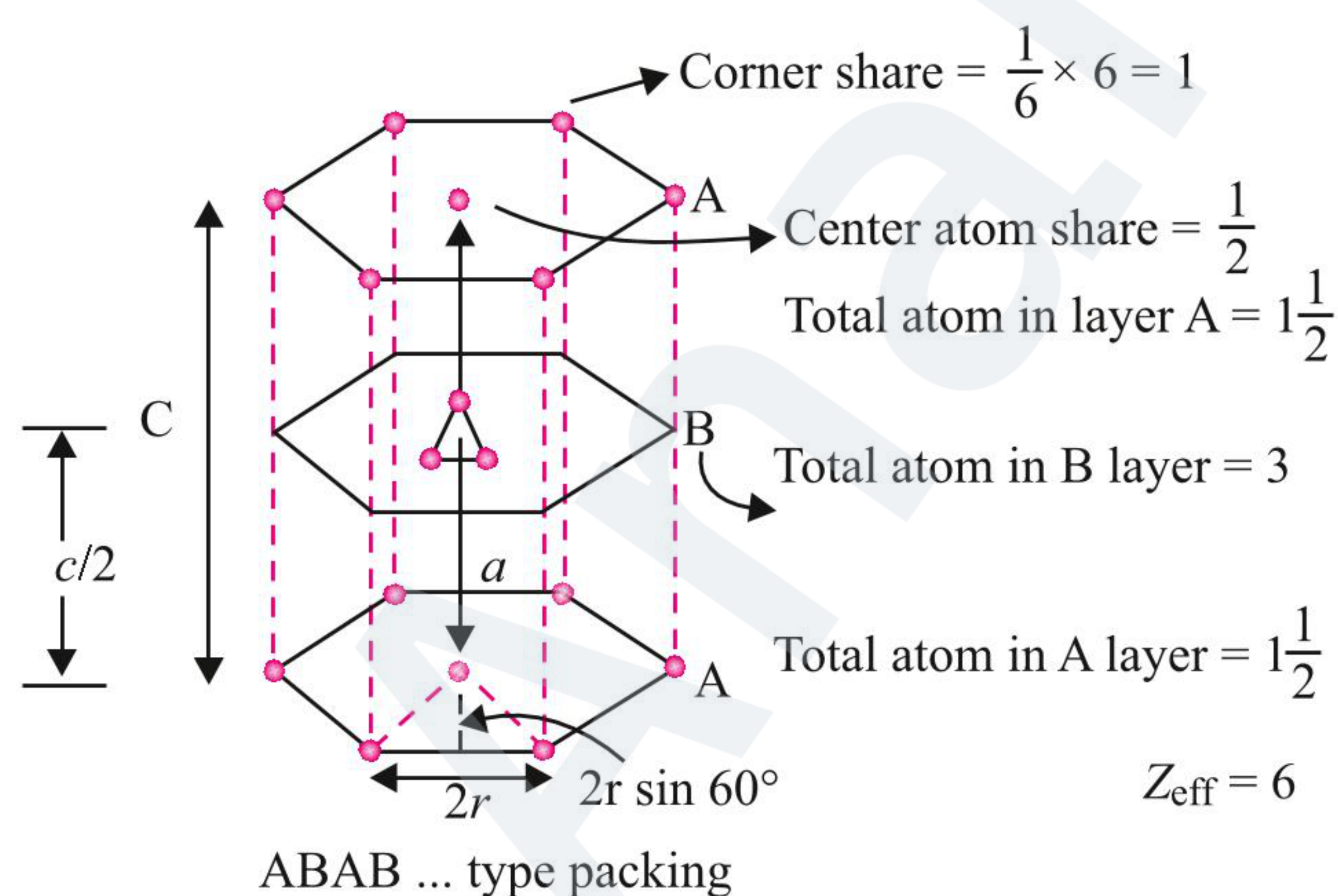
The packing ABAB... is known as hcp packing. The unit cell of hcp is shown in Figs. 1.61(a) and 1.61(b).



Exploded view

Hexagonal close-packed

(a)



(b)

Fig. 1.62 ABAB... type packing

a. Number of effective atoms per unit cell

- Three atoms in B layer exclusively belong to this prism (i.e., in the body centre of hexagonal)
- In layer A:
 - One atom in the centre is shared by two prisms.
 - There are 12 atoms in two A layers and each is shared

amongst six prisms of this type = $12 \times \frac{1}{6} = 2$

Z_{eff} in both A layers = $2 + 1 = 3$.

- Z_{eff} in two A layers + Z_{eff} in B layer = $3 + 3 = 6$
 $\therefore Z_{\text{eff}}$ in hcp = 6

Alternatively

$$Z_{\text{eff}}/\text{unit cell} = 12 \times \frac{1}{6} \text{ (corner) (from both A layer)} \\ + 2 \times \frac{1}{2} \text{ (in the centre of both A layers)} \\ + 3 \text{ (in the body in layer B)} = 6$$

b. Base area (A) of unit cell of hcp

It is equal to area of six equilateral triangles each with side $2r$ and altitude (Fig. 1.63).

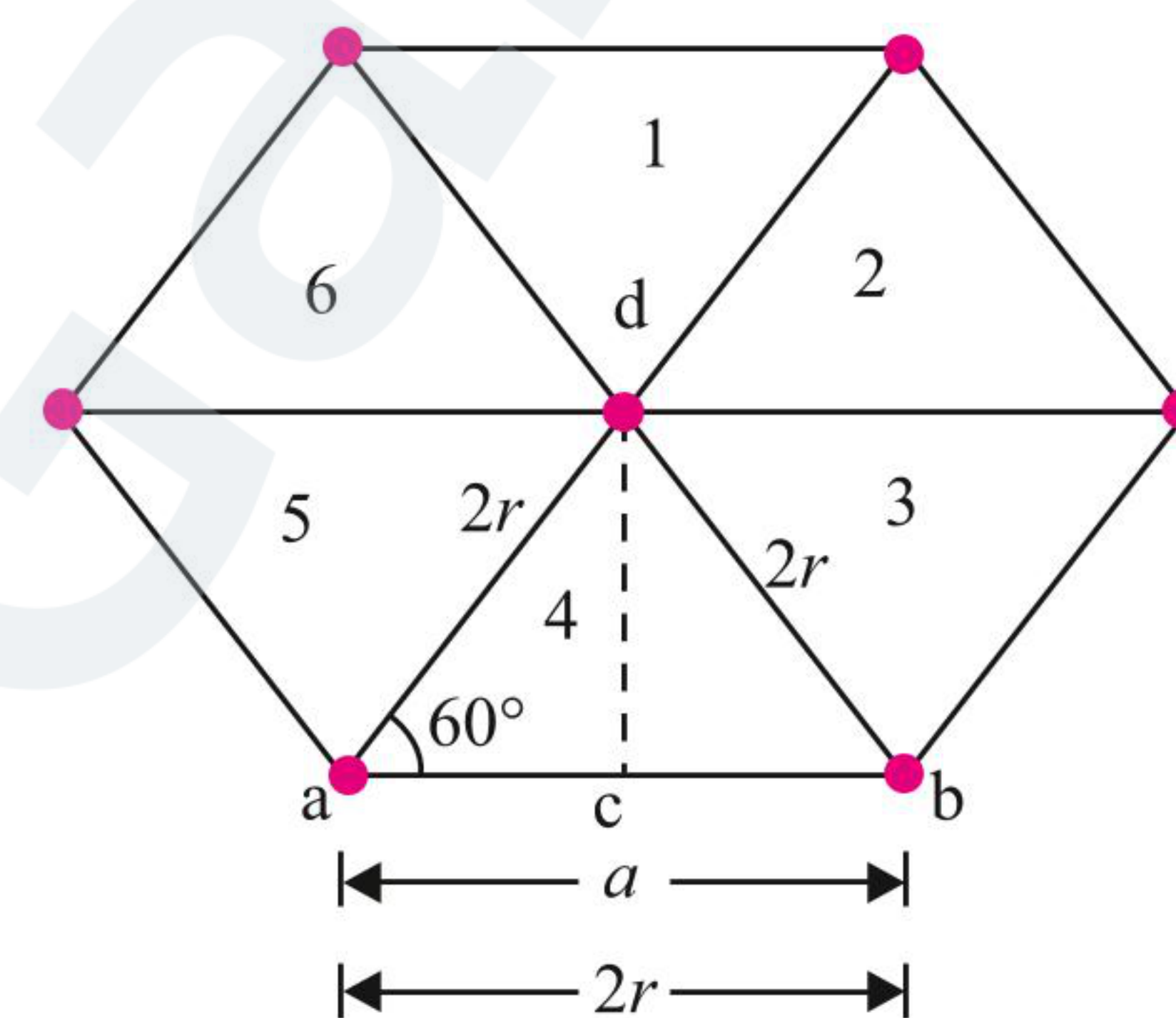


Fig. 1.63

$$\sin 60^\circ = \frac{\text{Perpendicular}}{\text{Hypotenuse}} = \frac{cd}{ad}$$

$$\therefore P(\text{altitude}) = 2r \times \frac{\sqrt{3}}{2} = \sqrt{3}r$$

$$\text{Base area, } A = 6 \times \frac{1}{2} (2r) \times \sqrt{3}r = 6\sqrt{3}r^2$$

(Learn it as a result.)

c. Calculation of height (c)

$c = 2 \times \text{Distance between close-packed layers}$

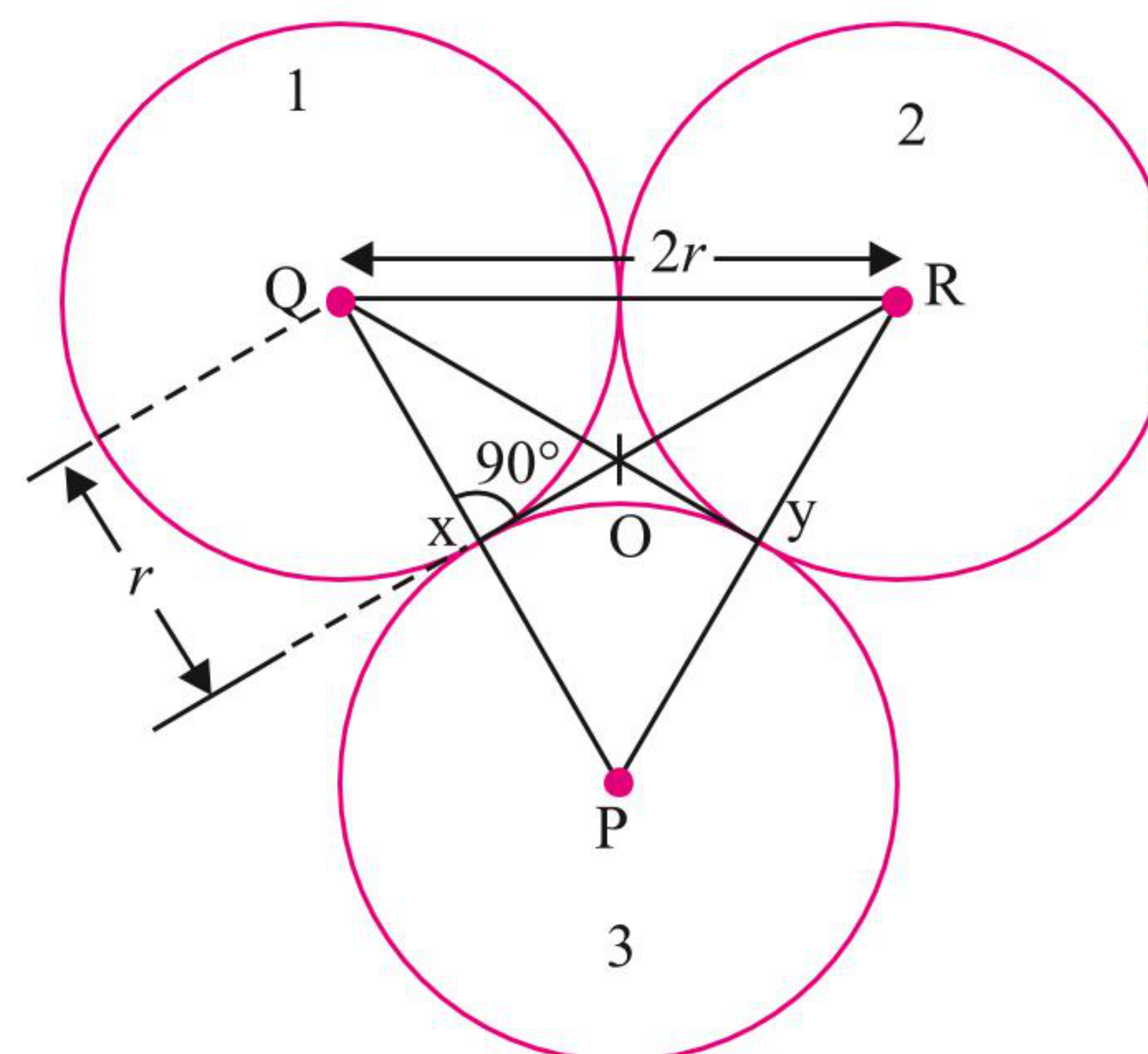


Fig. 1.64

- Let us take three balls (1, 2, and 3) in the base layer A. Out of three medians in an equilateral ΔPQR , two medians Qy and Rx are shown in Fig. 1.64 intersecting at point O.

- ii. In an equilateral Δ , medians are also perpendicular bisectors of sides, $\angle QxR = 90^\circ$ and Qx and $Ry = r$. In ΔQxR ,

$$(QR)^2 = (Qx)^2 + (xR)^2$$

$$(2r)^2 = r^2 + (xR)^2 \Rightarrow xR = \sqrt{3}r$$

- iii. Since medians intersect each other in the ratio of 2 : 1, thus

$$RO = \frac{2}{3} xR \Rightarrow RO = \frac{2}{3} \sqrt{3}r = \frac{2r}{\sqrt{3}}$$

- iv. Since distance between two layers A and B = $c/2$.

$\therefore$ In Fig. 1.65, point O is the intersection of medians.

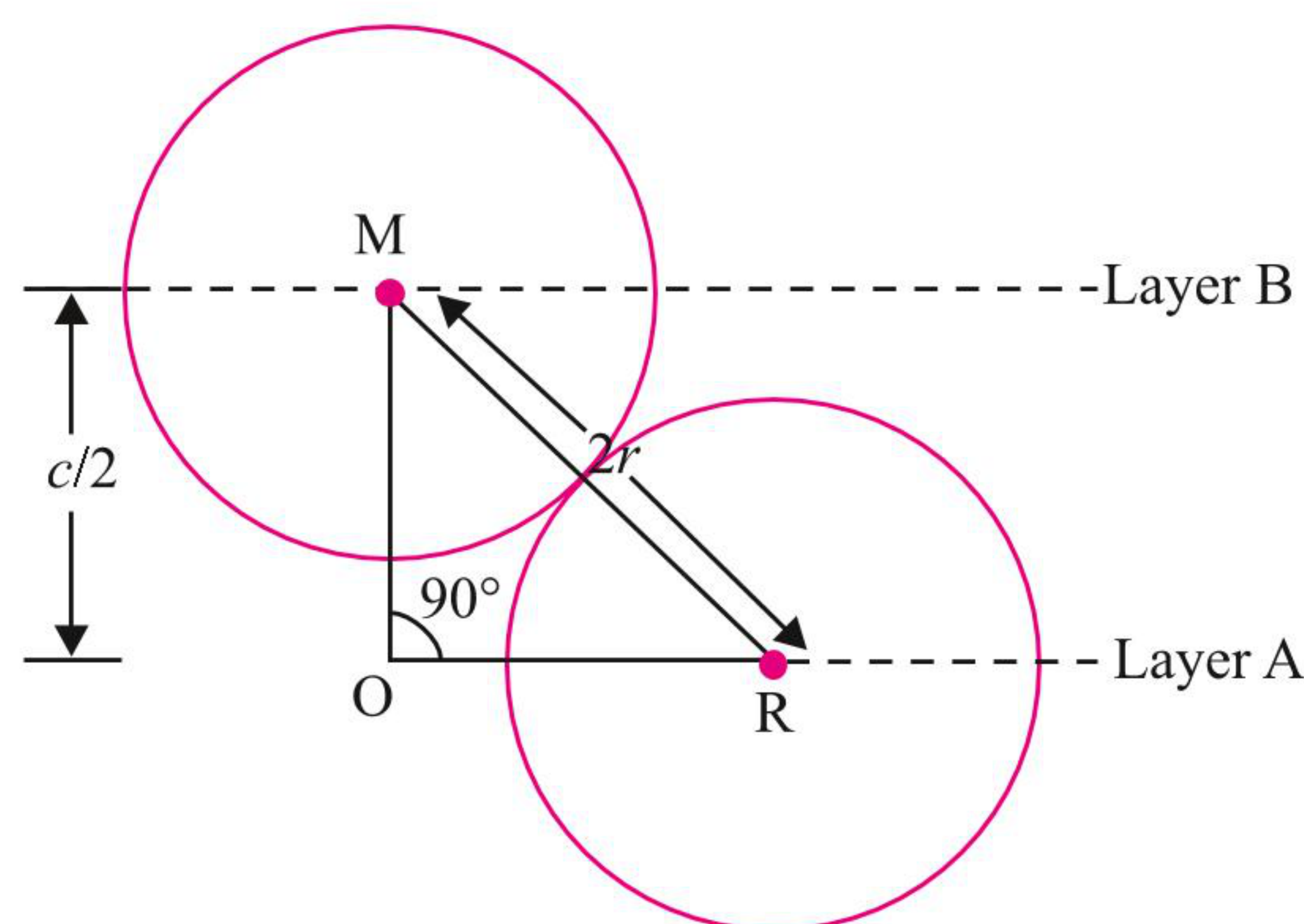


Fig. 1.65

In ΔMOR ,

$$(OM)^2 + (RO)^2 = (MR)^2$$

$$\left(\frac{c}{2}\right)^2 + \left(\frac{2r}{\sqrt{3}}\right)^2 = (2r)^2$$

$$\Rightarrow \left(\frac{c}{2}\right)^2 = \frac{8r^2}{3} \Rightarrow c = 4r \sqrt{\frac{2}{3}}$$

$$\text{Hence, height } (c) = 4r \times \sqrt{\frac{2}{3}} \text{ or } 2a \times \sqrt{\frac{2}{3}} \quad (\because a = 2r)$$

(Learn it as a result.)

- d. Volume of unit cell = Base area $\times$ Height (c)

$$= 6\sqrt{3}r^2 \times 4r \times \sqrt{\frac{2}{3}} = 24\sqrt{2}r^3$$

(Learn it as a result.)

- e. Packing fraction = $\frac{6 \times \text{Volume of atom}}{\text{Volume of unit cell}}$

$$= \frac{6 \times \frac{4}{3} \pi r^3}{24\sqrt{2}r^3} = \frac{\pi}{3\sqrt{2}} = \frac{3.143}{3 \times 1.414} = 0.74$$

$\therefore$ Packing efficiency = Packing fraction $\times 100$

(or % of volume occupied) = $0.74 \times 100 = 74\%$

% of volume unoccupied (empty space) = $100 - 74 = 26\%$

(Learn it as a result.)

- f. Calculation of c/a ratio for ideally close-packed hcp crystal:

$$\text{From the above in point c (iv), } c = 4r \sqrt{\frac{2}{3}} \quad (\because a = 2r)$$

$$\therefore \frac{c}{a} = \frac{4r}{2r} \sqrt{\frac{2}{3}} = 2 \times \sqrt{\frac{2}{3}} = 1.633$$

(Learn it as a result.)

Alternatively

The ABAB... type of stacking represents the hcp structure joining the centres of three neighbouring atoms of the middle plane to the centres of the atoms of the top and bottom planes resulting in two tetrahedra with a common base (Fig. 1.66). The top and bottom atoms are centres at two lattice points, one above the other on the two hexagonal base planes of the unit cell. So, the distance between them is the unit distance along the c -axis. The distance between any two adjacent atoms of a plane is unit distance along the a -axis. Unit of c is equal to twice the normal from the apex of a tetrahedron to its base. The unit of a is equal to the side of the tetrahedron.

$$\frac{c}{a} = \frac{2PT}{RS}$$

$$RU = \sqrt{RS^2 - SU^2} = \sqrt{a^2 - (a^2/4)} = \sqrt{3}a/2$$

$$RT = \frac{2}{3} RU = \frac{a}{\sqrt{3}}$$

$$PT = \sqrt{PR^2 - RT^2} = \sqrt{a^2 - (a^2/3)} = a\sqrt{2}/\sqrt{3}$$

$$\frac{c}{a} = \frac{2\sqrt{2}}{\sqrt{3}} = 1.633$$

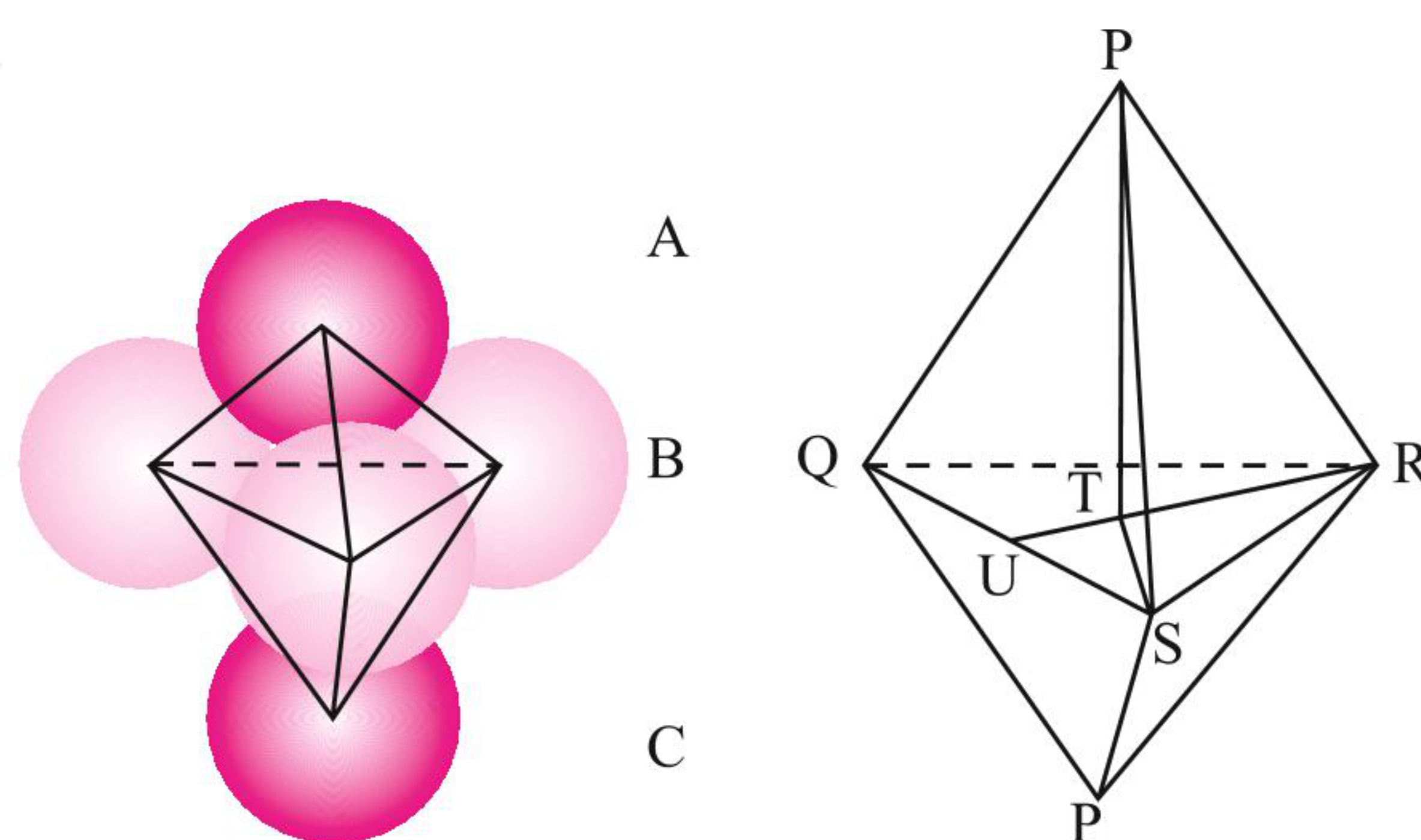


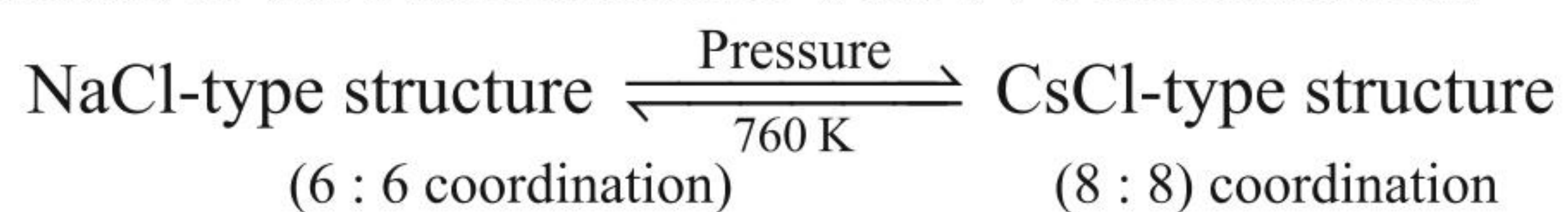
Fig. 1.66 In the ABAB... packing, which is hcp, the centres of three atoms Q, R, and S on plane B are joined to the centres of P atoms in plane A above and below

1.23 EFFECT OF TEMPERATURE AND PRESSURE ON A CRYSTAL STRUCTURE

A number of metals have more than one crystal form, iron, for example, is bcc at room temperature and changes over to the fcc form at 910°C . At 1410°C , iron again changes over to the bcc form. In general, at higher temperatures, bcc crystal structure is to be expected as it allows larger vibrational amplitudes for atoms, thereby increasing the entropy and lowering the free energy of the crystal. This is believed to be the reason for a number of alkali metals adopting the bcc form at room temperature.

At ordinary temperatures and pressures, chlorides, bromides, and iodides of lithium, sodium, and rubidium and some halides of silver possess the NaCl structure with 6 : 6 coordination. On the application of high pressure, they transform to the CsCl structure

with 8 : 8 coordination. On the other hand, CsCl on heating transforms to the NaCl structure with 6 : 6 coordination.

**ILLUSTRATION 1.30**

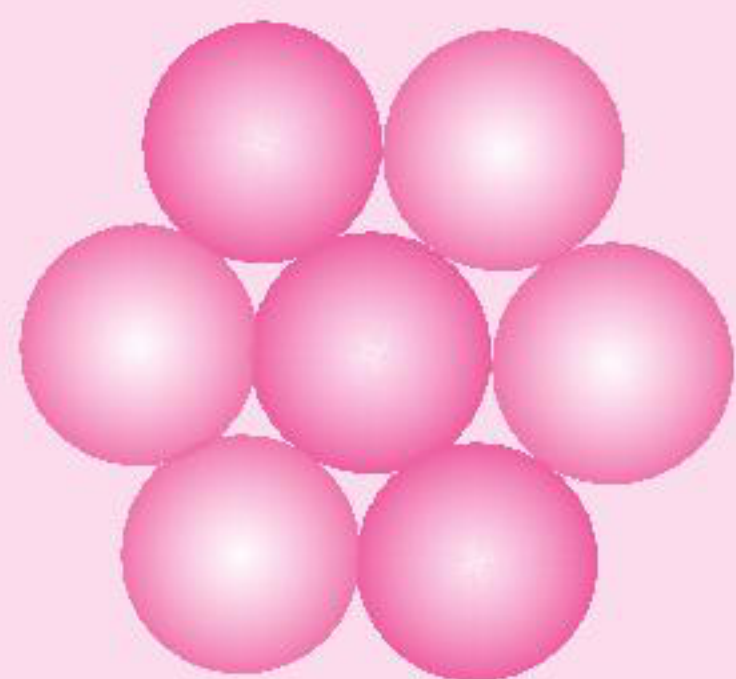
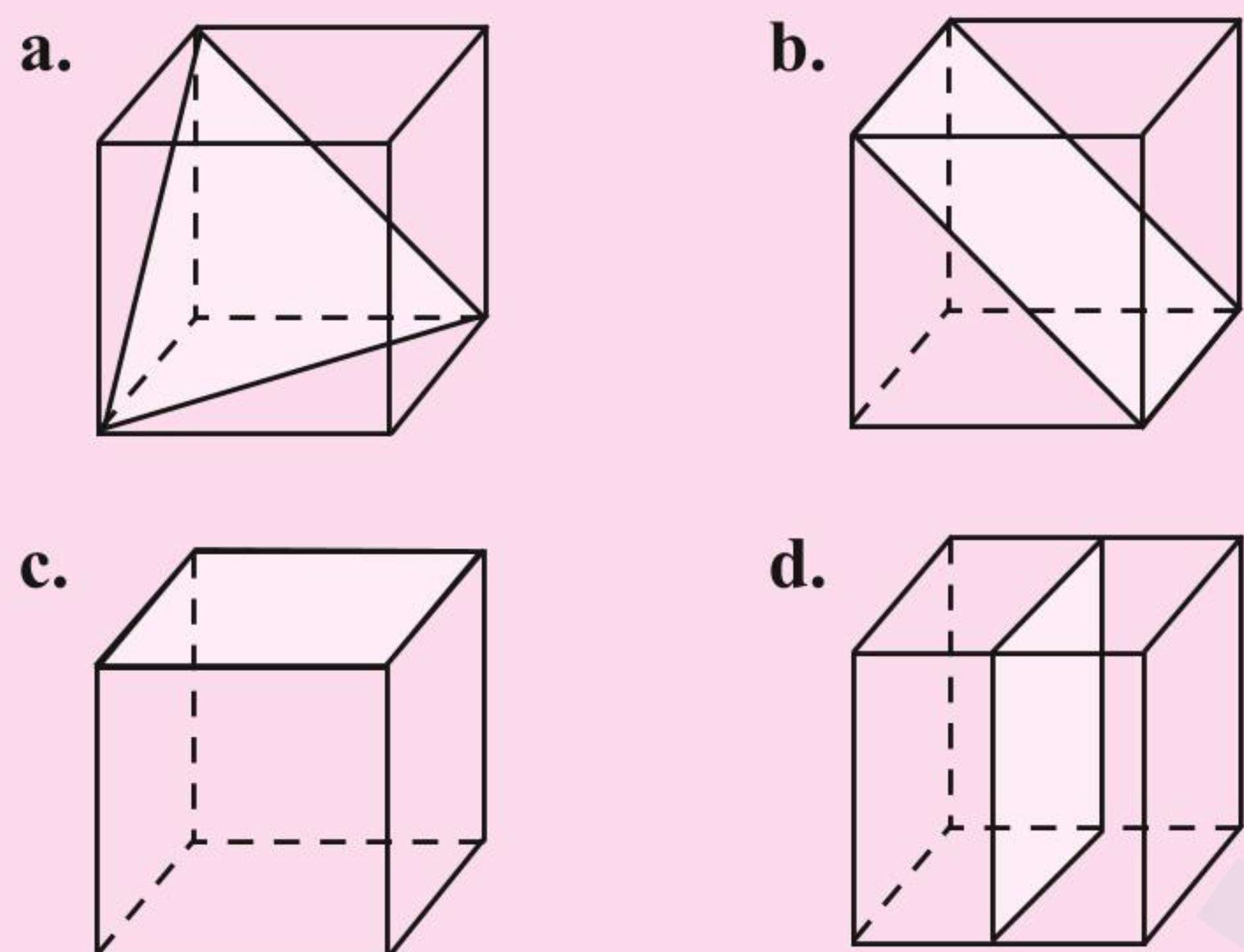
Whenever a two-dimensional square packing same layers are kept in the way so that the centres are aligned in all three dimensions, coordination number of each sphere is

- a. 6 b. 8 c. 12 d. 10

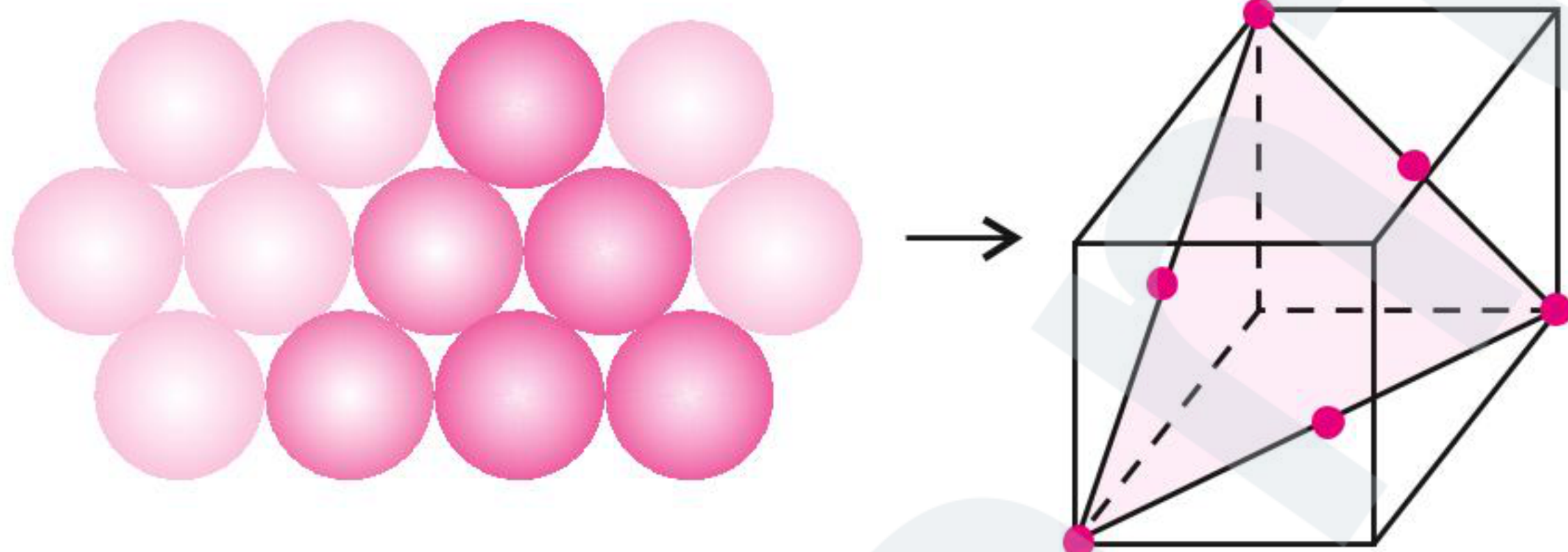
Sol. a. The coordination number is 6. ("4 atoms" in the plane + 1 atom above + 1 atom below the particular atom).

ILLUSTRATION 1.31

In an fcc crystal, which of the following shaded planes contain the given ($\rightarrow$) type of arrangement of atoms?



Sol. a.

**ILLUSTRATION 1.32**

In hexagonal close packing of sphere in three dimensions.

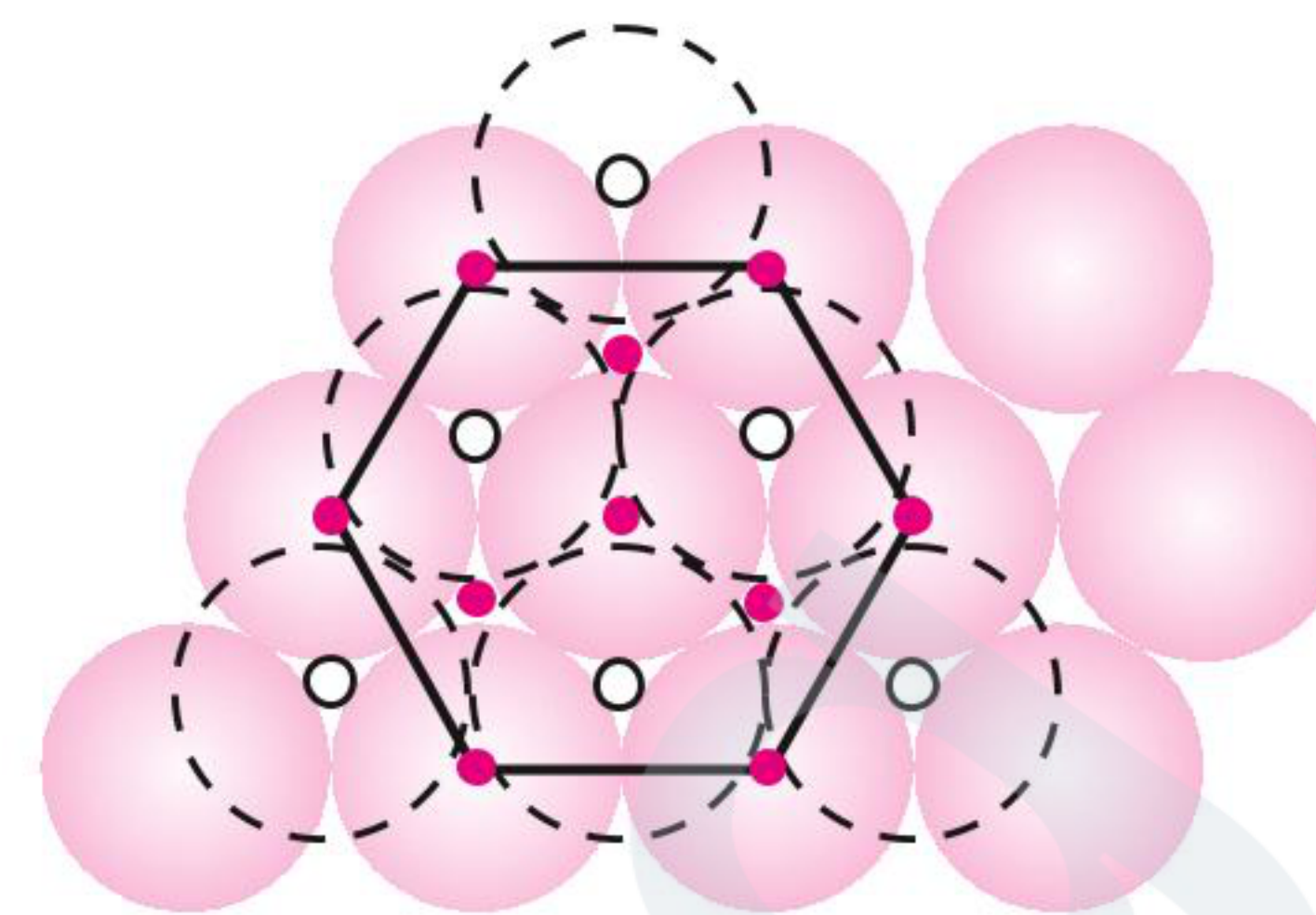
- In one unit cell there are 12 octahedral voids and all are completely inside the unit cell.
- In one unit cell there are six octahedral voids and all are completely inside the unit cell.
- In one unit cell there are six octahedral voids and of which three are completely inside the unit cell and other three are from contributions of octahedral voids which are partially inside the unit cell.
- In one unit cell there are 12 tetrahedral voids, all are completely inside the unit cell.

Sol. b. hcp = AB AB AB... pattern repeat

For calculating voids between two layers A and B,

Total tetrahedral voids = 12 (represented by "o") out of which 8 are completely inside but rest are shared by other unit cells.

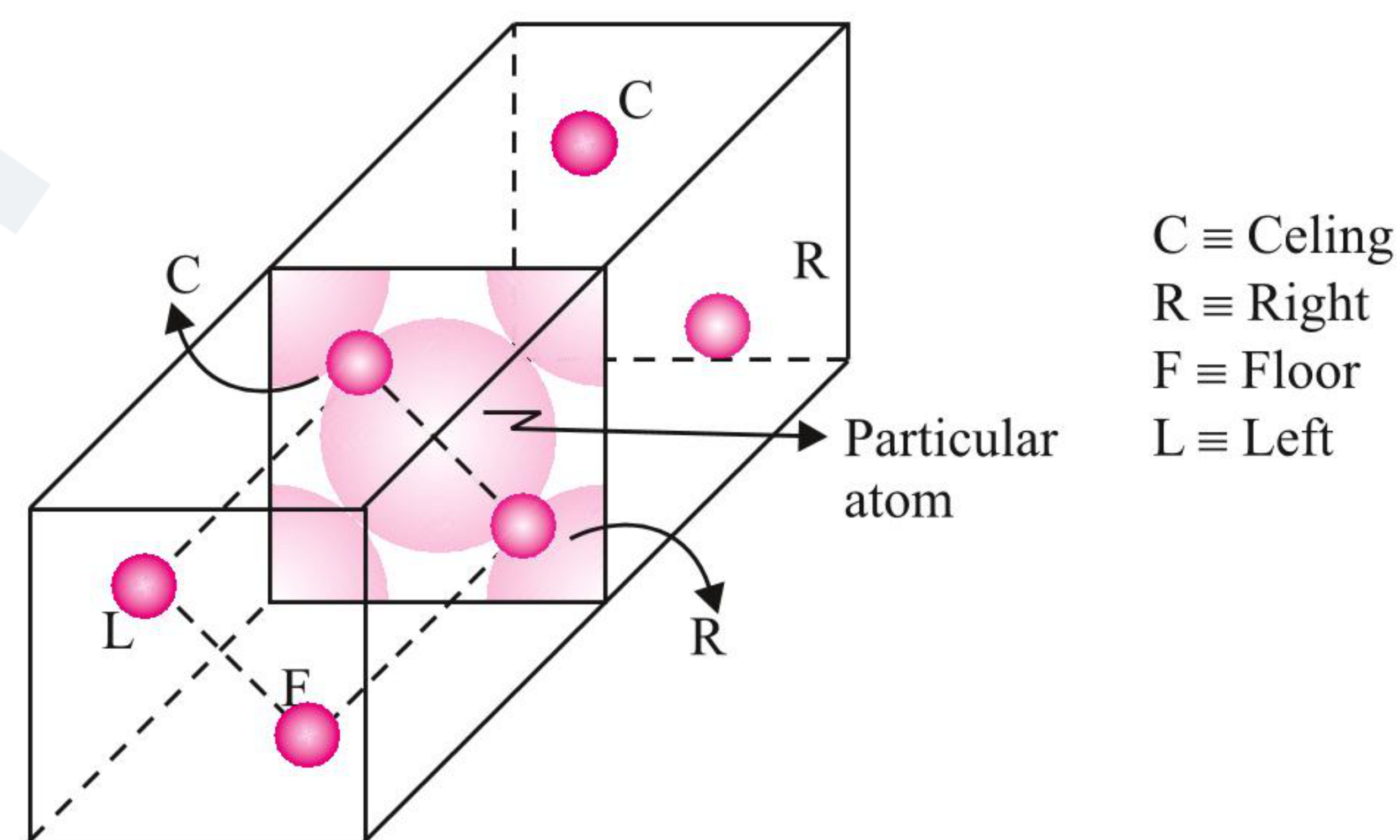
Total octahedral voids = 6 (represented by "●"). All are completely inside.

**ILLUSTRATION 1.33**

The coordination number of an fcc structure for a metal is 12, since

- Each atom touches four others in same layer, two in layer above and six in layer below.
- Each atom touches four others in same layer, four in layer above and four in layer below.
- Each atom touches six others in same layer, three in layer above and three in layer below.
- Each atom touches eight others in same layer, two in layer above and two in layer below.

Sol. a.



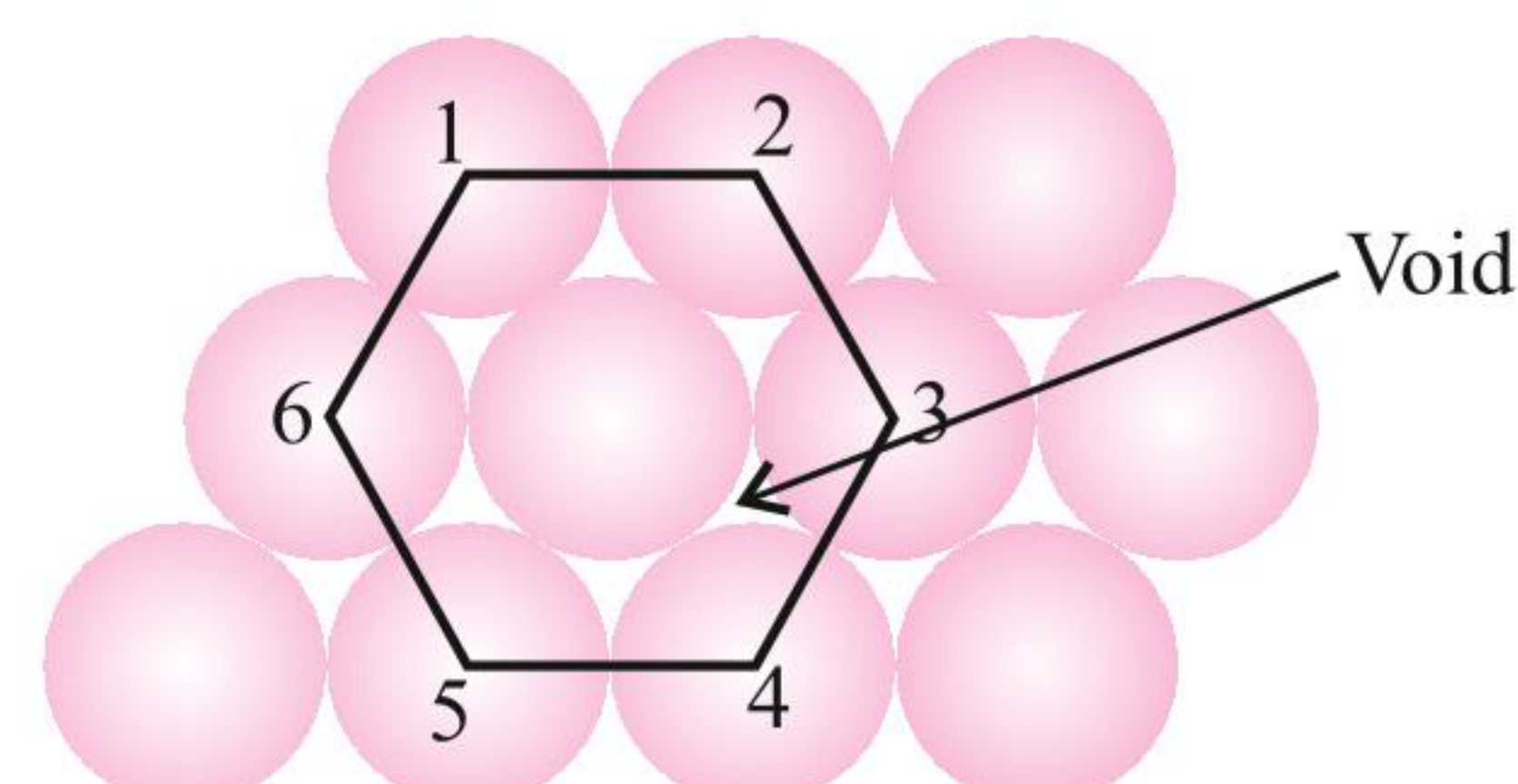
Each atom touches 4 atoms in the same layer, 4 in above layer and 4 in layer below.

ILLUSTRATION 1.34

Which of the following statements is correct for a two-dimensional hexagonal close-packed layer?

- Each sphere is surrounded by six spheres
- Each sphere is surrounded by six voids
- Each sphere has three voids
- Each void is surrounded by three spheres

Sol. (a, b, d)



- Each sphere is surrounded by six spheres.
- Each sphere is surrounded by six voids.
- Effective number of atoms in a hexagonal unit cell

$$= \left(\frac{1}{3} \times 6 \right) \times (1 \times 1) = 3$$

Effective number of voids in a hexagonal unit cell = 6

Hence, each sphere has two voids.

- Each void is surrounded by three spheres.

ILLUSTRATION 1.35

A compound made of particles A, B, and C forms ccp lattice. Ions A are at lattice points, B occupy TVs and C occupy OVs. If all the ions along one of the edge axis are removed, then the formula of the compound is

- | | |
|--------------------------|---------------------|
| a. $A_{3.75}B_8C_{3.75}$ | b. $A_{3.75}B_4C_8$ |
| c. $A_4B_8C_{3.75}$ | d. $A_4B_{3.75}C_8$ |

Sol. a. Since lattice is ccp, $Z_{\text{eff}} = 4$.

$\therefore$ Number of A ions = 4

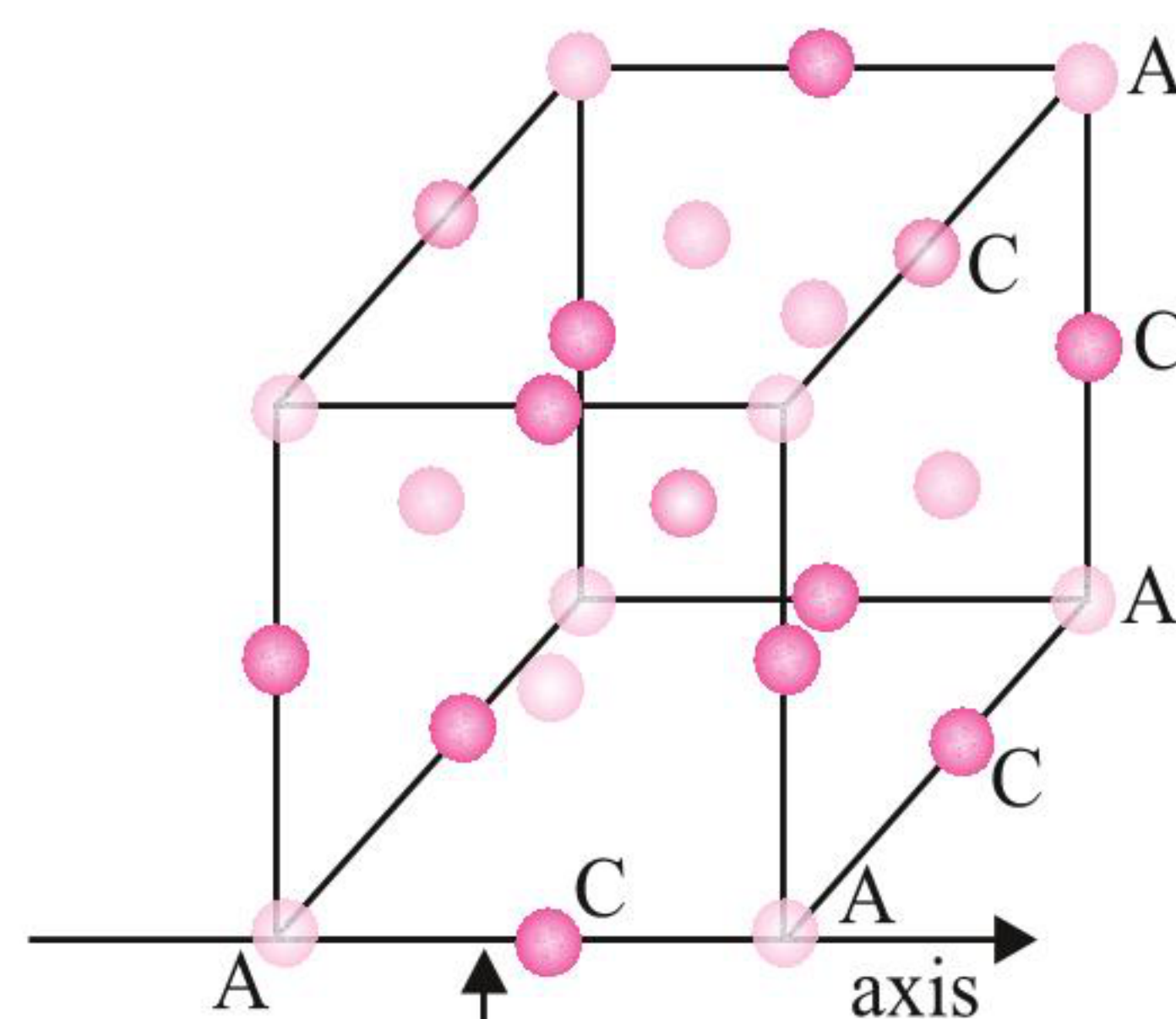
(corner + face centre = $1 + 3 = 4$)

Number of B ions = Number of TVs = 8

Number of C ions = Number of OVs = 4

2 TVs are formed at each body diagonal of cube.

4 TVs are formed on edge centres and body centre.



(Axis passing through one of the edges)

- A ions are at corner + face center
- C ions are at edge center and body center (where OVs are formed)
- 2 B ions (not shown in the figure) are at four-body diagonal

2 A ions (at corner) and one C ion (at edge centre) are removed.

$$\text{Number of A ions removed} = 2 \times \frac{1}{8} \text{ (corner share)} = \frac{1}{4}$$

$$\begin{aligned} \text{Number of C ions removed} &= 1 \times \frac{1}{4} \text{ (edge centre share)} \\ &= \frac{1}{4} \end{aligned}$$

$$\text{Number of A ions left} = 4 - \frac{1}{4} = 3.75$$

Number of B ions = 8

(Since no B ion has been removed)

$$\text{Number of C ions left} = 4 - \frac{1}{4} = 3.75$$

Thus, formula is: $A_{3.75}B_8C_{3.75}$

ILLUSTRATION 1.36

A compound made of particles A, B, and C forms ccp lattice. In the lattice, ions A occupy the lattice points and ions B and C occupy the alternate TVs. If all the ions along one of the body diagonals are removed, then formula of the compound is

- | | |
|---------------------|---------------------|
| a. $A_{3.75}B_3C_3$ | b. $A_{3.75}B_3C_4$ |
| c. $A_3B_{3.75}C_3$ | d. $A_3B_3C_{3.75}$ |

Sol. a. Since the lattice is ccp ($Z_{\text{eff}} = 4$).

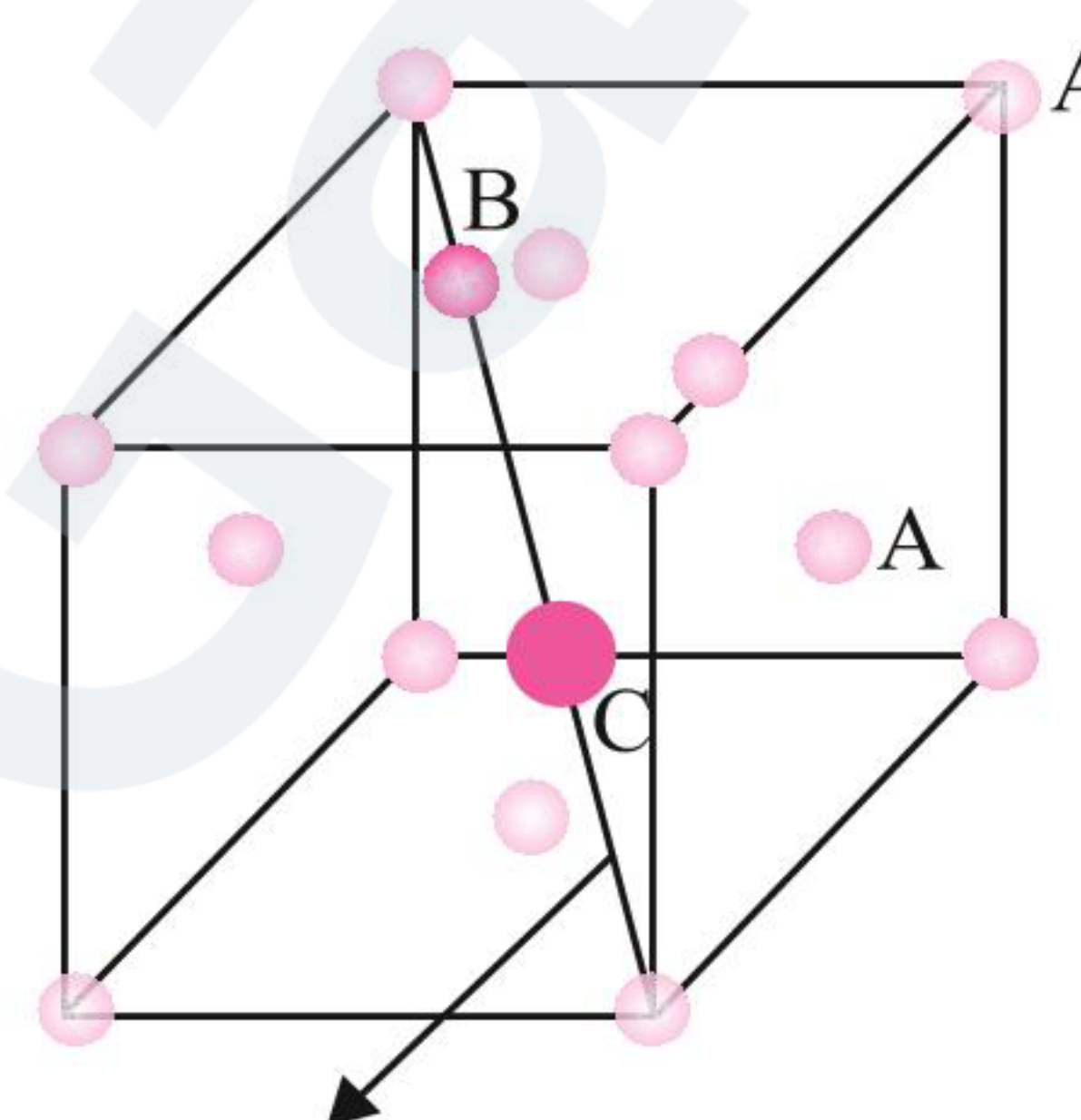
$\therefore$ Number of A ions = 4

(corner + face centre = $1 + 3 = 4$)

Number of B ions = Number of alternate TV = 4

Number of C ions = Number of alternate TV = 4.

$$\text{Number of A ions removed} = 2 \times \frac{1}{8} \text{ (corner share)} = \frac{1}{4}$$



One of the body diagonals. Other diagonals are not shown in the figure

- A ions are at corner + face center
- B ions are at alternate TV at each of the 4 body diagonal
- C ions are also at alternate TVs at each of the four body diagonals

Number of B ions removed = 1

Number of C ions removed = 1

(Since body diagonal ions are inside the cube so they do not share with other ions).

$$\text{Number of A ions left} = 4 - \frac{1}{4} = 3.75$$

$$\text{Number of B ions left} = 4 - 1 = 3$$

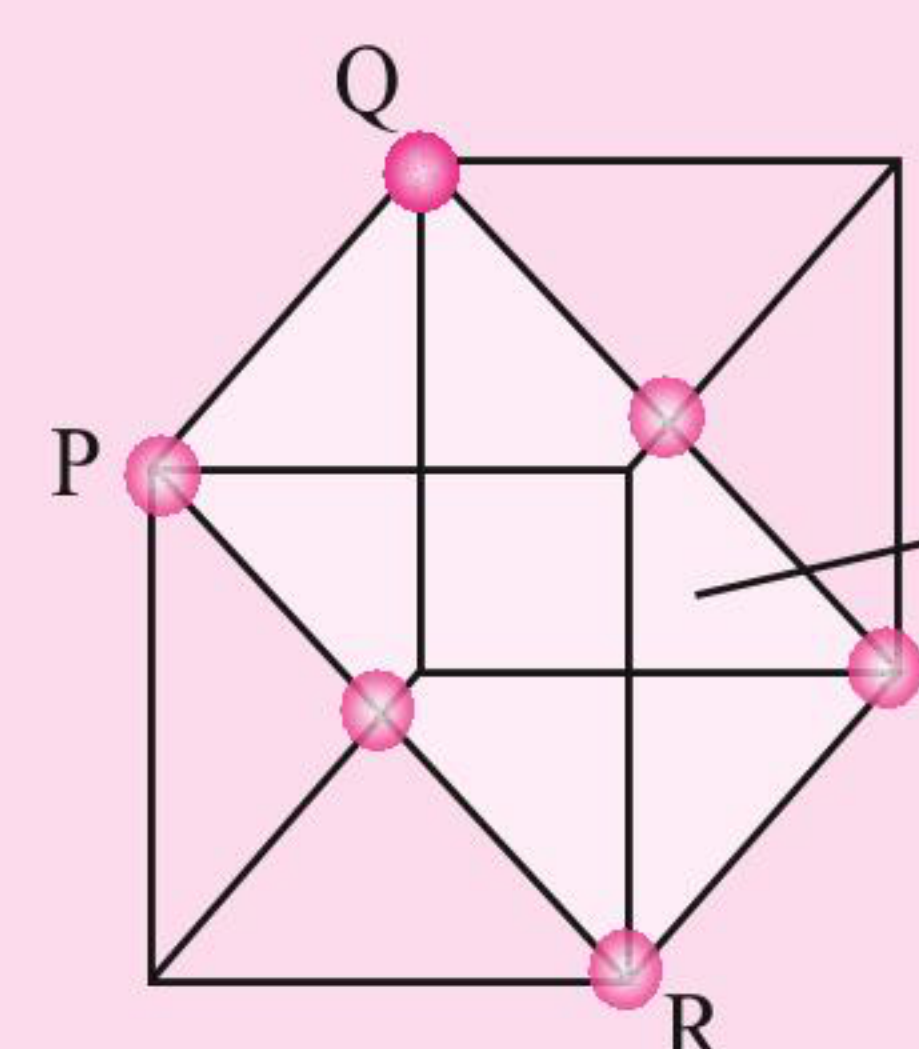
$$\text{Number of C ions left} = 4 - 1 = 3$$

Thus, formula is: $A_{3.75}B_3C_3$

ILLUSTRATION 1.37

A compound is made of particles A and B. A forms fcc packing and B occupies all the OVs. If all the particles along the plane as shown in the figure below are removed, then the simplest formula of the compound is

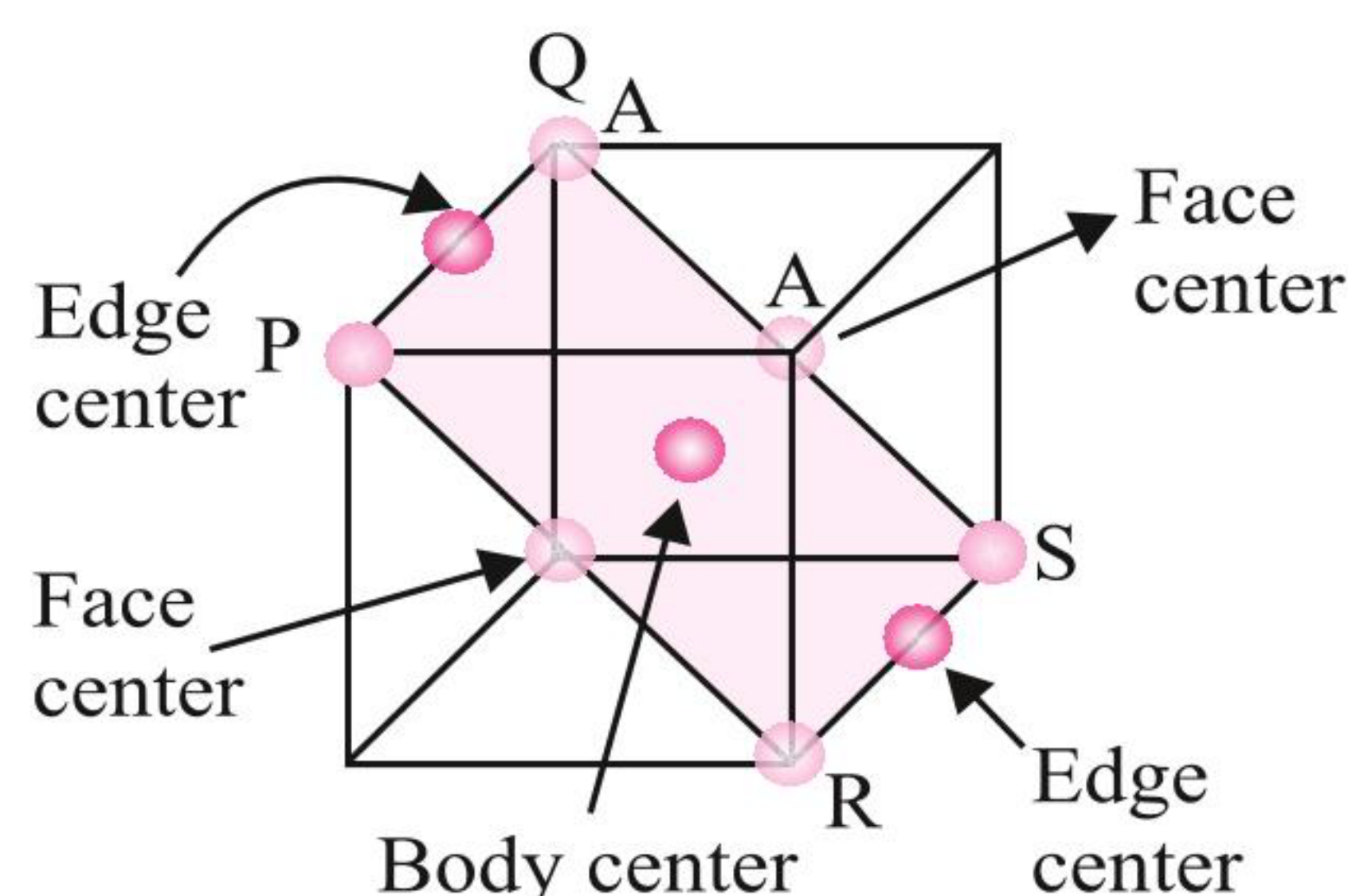
- | | | | |
|-------------|-------------|-------|----------------|
| a. A_5B_7 | b. A_7B_5 | c. AB | d. $AB_{3.75}$ |
|-------------|-------------|-------|----------------|



Plane from where the ions are removed, (other ions are not shown, visualize yourself)

Sol. c. Since the lattice is fcc ($Z_{\text{eff}} = 4$), therefore, number of A ions = 4 (1 corner + 3 face centre)
 Number of B ions = Number of OVs = 4.
 (OVs are formed at body centre and edge centre).
 Ions are removed from the plane (PQRS) as shown in the figure. From the figure, it is clear, 4 corner ions and two edge centre ions on PQ and RS are also removed. Also two face centre ions lying on PR and QS along with one ion present in the body centre are removed as shown in the figure below.

b.



- 4 A ions from corner and 2 A ions from face center (PR and QS are removed)
- 2 B ions from edge center (PQ and RS) and one ion from body center are removed

∴ Number of A ions removed

$$= 4 \times \frac{1}{8} (\text{corner share}) + 2 \times \frac{1}{2} (\text{face centre share})$$

$$= \frac{1}{2} + 1 = 1\frac{1}{2}$$

Number of B ions removed

$$= 2 \times \frac{1}{4} (\text{edge centre share}) + \frac{1}{1} (\text{body centre share})$$

$$= \frac{1}{2} + 1 = 1\frac{1}{2}$$

$$\text{Number of A ions left} = 4 - 1\frac{1}{2} = 2.5$$

$$\text{Number of B ions left} = 4 - 1\frac{1}{2} = 2.5$$

$$\text{Thus, formula} = A_{2.5}B_{2.5} = 2.5AB$$

Simplest formula = AB

ILLUSTRATION 1.38

In a solid having rock salt structure, if all the atoms touching one body diagonal plane are removed (except at body centre), then the formula of the left unit cell is

- | | |
|---------------------|-------------|
| a. $A_{3.5}B_{2.5}$ | b. A_7B_3 |
| c. A_5B_3 | d. A_3B_5 |

Sol. a. NaCl (rock salt)-type structure is fcc type.

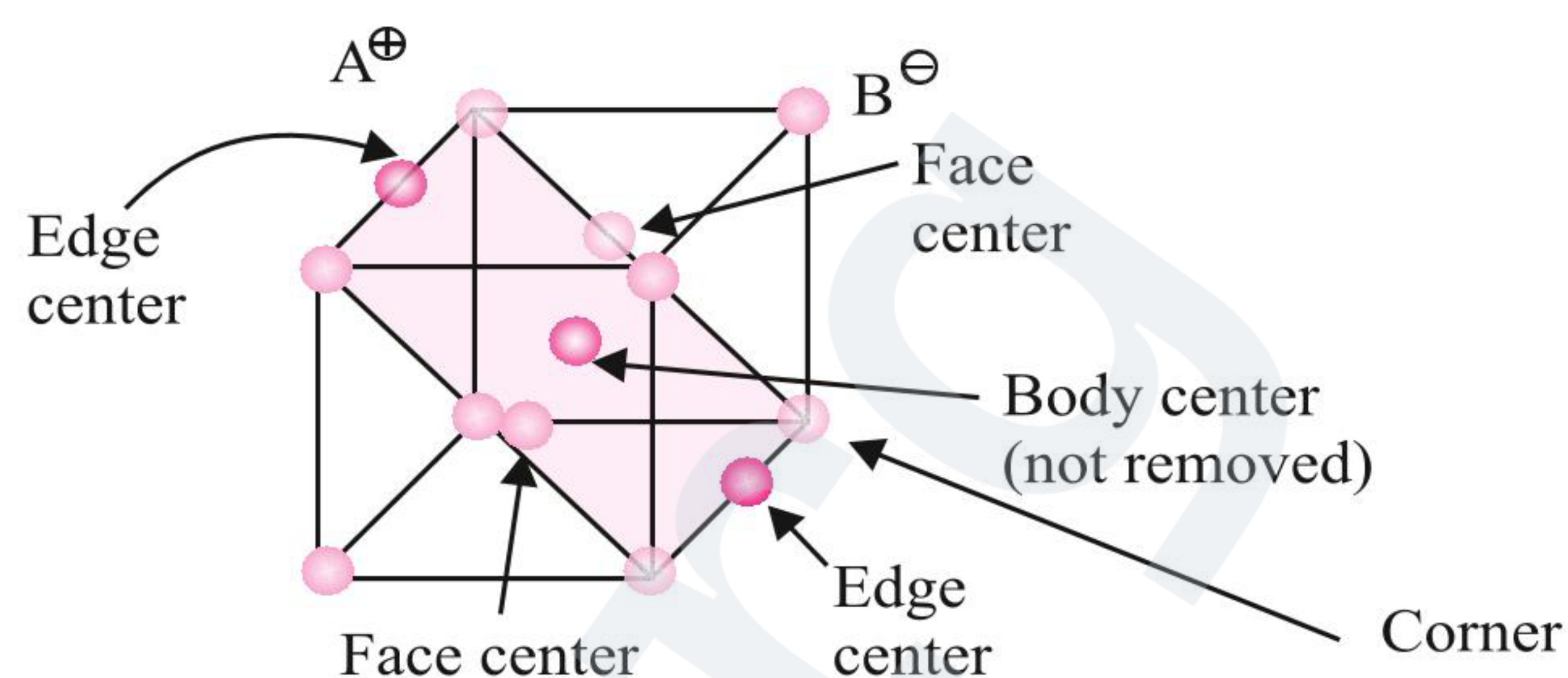
$$(\therefore Z_{\text{eff}} = 4) \quad [Z_{\text{eff}}(\text{Na}^+) = 4, Z_{\text{eff}}(\text{Cl}^-) = 4]$$

In NaCl structure anion (Cl^-) (here B^-) are present at corners and face centre while cations (Na^+) (here A^+) are present in all OVs (present at body centre and edge centre).

∴ Number of B^- ions removed

$$= 4 \times \frac{1}{8} (\text{corner share}) + 2 \times \frac{1}{2} (\text{face centre share})$$

$$= \frac{1}{2} + 1 = 3/2$$



- 4 B^- from corner and 2 B^- from face center are removed
- 2 A^+ from edge center are removed (body centered is not removed)

$$\text{Number of } \text{A}^+ \text{ ions removed} = 2 \times \frac{1}{4} (\text{edge centre share}) = \frac{1}{2}$$

Note: Body centre A^+ ion is not removed.

$$\therefore \text{Number of } \text{B}^- \text{ ions left} = 4 - \frac{3}{2} = \frac{5}{2} = 2.5$$

$$\text{Number of } \text{A}^+ \text{ ions left} = 4 - \frac{1}{2} = \frac{7}{2} = 3.5$$

Thus, formula is: $\text{A}_{3.5}\text{B}_{2.5}$.

ILLUSTRATION 1.39

Calculate the value of Avogadro's number from the following data:

$$\text{Density of NaCl} = 2.165 \text{ g cm}^{-3}$$

$$\text{Distance between } \text{Na}^+ \text{ and } \text{Cl}^- \text{ in NaCl} = 281 \text{ pm}$$

Sol. A unit cell of NaCl contains four NaCl units.

$$\therefore Z_{\text{eff}} = 4, M_w = 23 + 35.5 = 58.5,$$

$$\rho = 2.165 \text{ g cm}^{-3} (\text{given})$$

$$\text{As distance between } \text{Na}^+ \text{ and } \text{Cl}^- \text{ in NaCl} = 281 \text{ pm}$$

$$\therefore \text{Edge of the unit cell} = 2 \times 281 = 562 \text{ pm}$$

Substituting these values in the expression

$$\rho = \frac{Z_{\text{eff}} \times M_w}{a^3 \times N_A \times 10^{-30}}$$

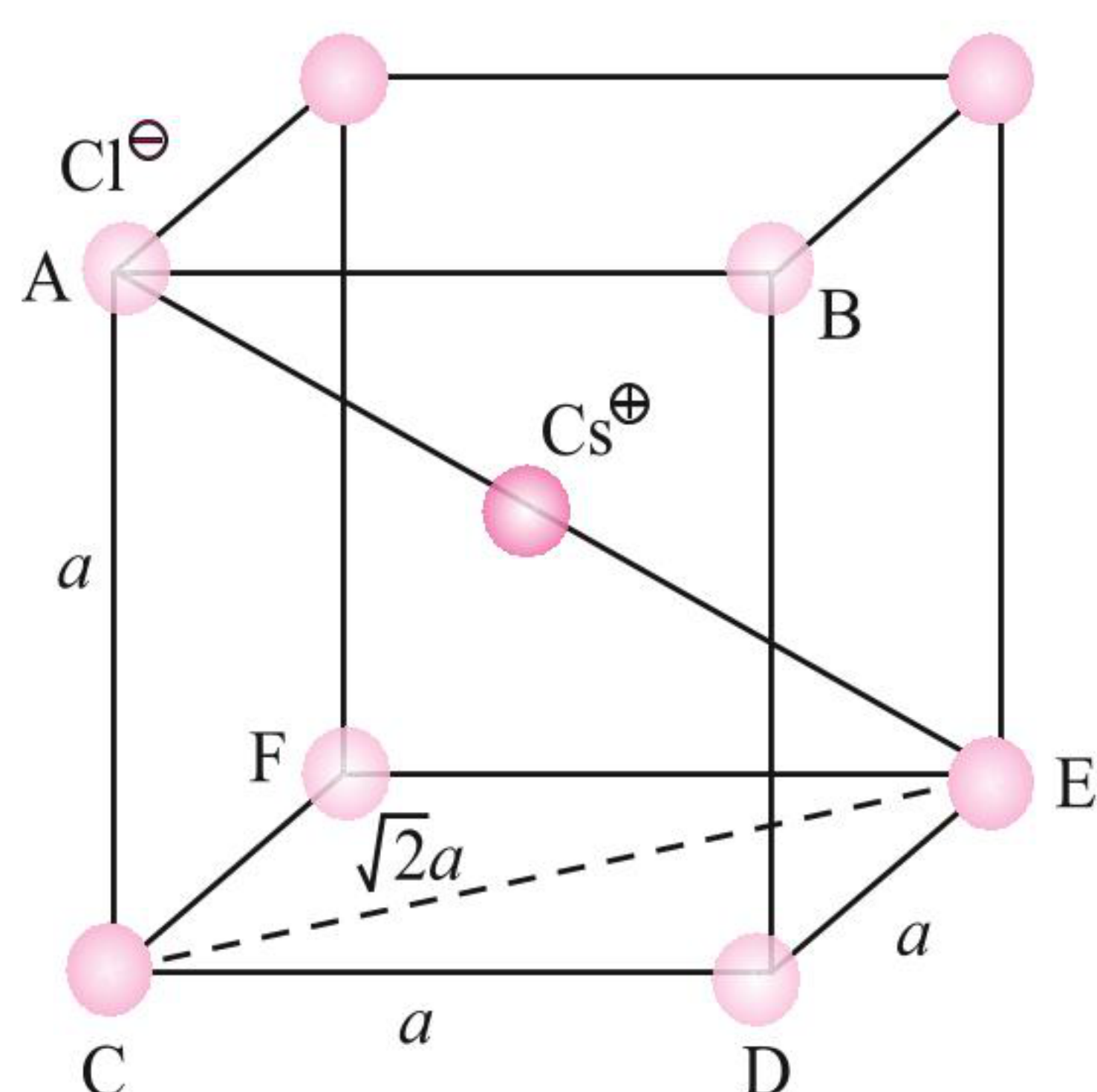
$$2.165 = \frac{4 \times 58.5}{(562)^3 \times N_A \times 10^{-30}}$$

$$N_A = 6.09 \times 10^{23}$$

ILLUSTRATION 1.40

CsCl has bcc arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl.

Sol. The bcc arrangement of CsCl is shown in the figure below. The aim is to find half of the body diagonal AE. If the edge of the unit cell is a , then



$$CE = \sqrt{a^2 + a^2} = \sqrt{2}a$$

$$\therefore AE = \sqrt{(\sqrt{2}a)^2 + a^2} = \sqrt{3}a$$

$$= \sqrt{3} \times 400$$

$$\therefore \text{Interionic distance} = \frac{1}{2} AE$$

$$= \frac{\sqrt{3}}{2} \times 400 = 346.4 \text{ pm}$$

ILLUSTRATION 1.41

A solid AB has CsCl-type structure. The edge length of the unit cell is 404 pm. Calculate the distance of closest approach between $A^{\oplus}$ and $B^{\ominus}$ ions.

Sol. The distance of closest approach is equal to the distance between the nearest neighbours (d). As CsCl has bcc lattice,

$$d = \frac{\sqrt{3}}{2} a = \frac{1.732}{2} \times 404 \text{ pm} = 349.9 \text{ pm}$$

ILLUSTRATION 1.42

CsCl has cubic structure. Its density is 3.99 g cm^{-3} . What is the distance between $\text{Cs}^{\oplus}$ and $\text{Cl}^{\ominus}$ ions? (Atomic mass of Cs = 133)

Sol. CsCl has bcc structure, so $Z_{\text{eff}} = 1$

$$\rho = \frac{Z_{\text{eff}} \times Mw}{a^3 \times 10^{-30} \times N_A} \text{ or } a^3 = \frac{Z_{\text{eff}} \times Mw}{\rho \times 10^{-30} \times N_A}$$

$$= \frac{1 \times (133 + 35.5)}{3.99 \times 10^{-30} \times 6.02 \times 10^{23}}$$

$$= 70.15 \times 10^6$$

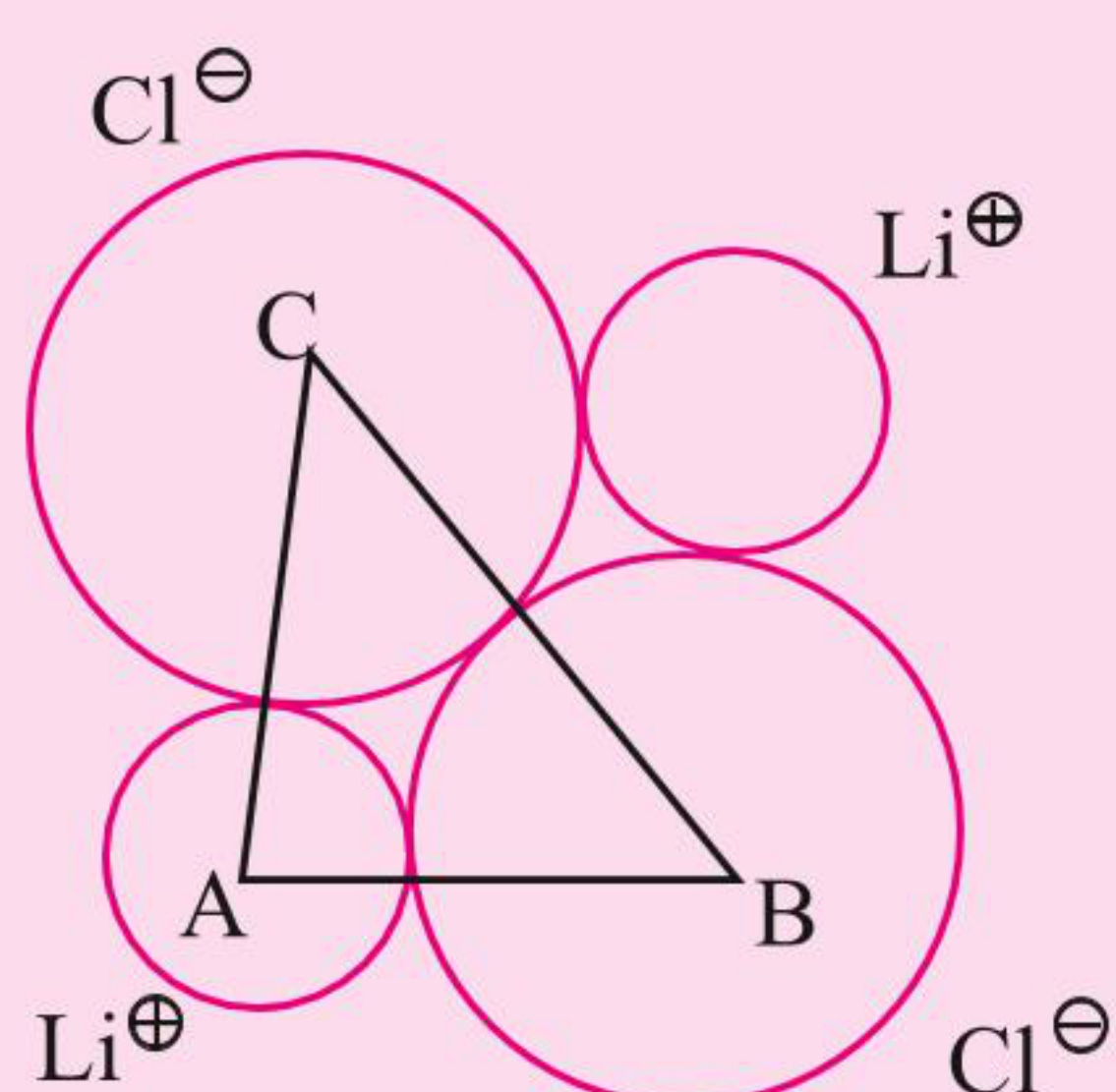
$$a = (70.15)^{1/3} \times 10^2$$

$$= 4.12 \times 10^2 \text{ pm} = 412 \text{ pm}$$

$$\text{Interionic distance} = \frac{\sqrt{3}a}{2} = \frac{1.732}{2} \times 412 = 356.8 \text{ pm}$$

ILLUSTRATION 1.43

The unit cube length for LiCl (NaCl structure) is $5.14 \text{ \AA}$. Assuming anion-anion contact, calculate the ionic radius for chloride ion.



Sol. Interionic distance of LiCl

$$= \frac{5.14}{2} = 2.57 \text{ \AA}$$

$$\therefore BC = \sqrt{AB^2 + AC^2} = \sqrt{(2.57)^2 + (2.57)^2} = 3.63$$

$$\text{Radius of } \text{Cl}^{\ominus} \text{ ion} = \frac{1}{2} \times 3.63 = 1.81 \text{ \AA}$$

ILLUSTRATION 1.44

Cesium may be considered to form interpenetrating simple primitive cubic crystal. The edge length of unit cell is 412 pm. Determine

- The density of CsCl.
- The ionic radius of $\text{Cs}^{\oplus}$ if the ionic radius of $\text{Cl}^{\ominus}$ is 181 pm. Given: $A_w(\text{Cs}) = 133 \text{ g mol}^{-1}$.

Sol. The interpenetrating simple primitive cubic crystals mean the unit cell is body-centred where $\text{Cl}^{\ominus}$ ions occupy corners and $\text{Cs}^{\oplus}$ ions occupy body centre of the cube. There is one $\text{Cs}^{\oplus}$ ion and one $\text{Cl}^{\ominus}$ ion (or one molecule of CsCl) per unit cell.

$$\text{From the expression, } \rho = \frac{Z_{\text{eff}} \times A_w}{a^3 \times N_A}$$

$$= \frac{1}{(412 \times 10^{-12} \text{ m})^3} \left(\frac{133.0 \text{ g mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} \right)$$

$$= 0.4 \times 10^7 \text{ g m}^{-3} \equiv 4.0 \text{ g cm}^{-3}$$

Now since $\text{Cs}^{\oplus}$ ions touch the two chlorides along the cross diagonal of the cube, we will have

$$2r_c + 2r_a = \sqrt{3}a$$

$$\text{or } r_c = \left(\frac{\sqrt{3}}{2} \right) a - r_a = \left(\frac{\sqrt{3}}{2} \right) (412 \text{ pm}) - (181 \text{ pm})$$

$$= 175.8 \text{ pm}$$

ILLUSTRATION 1.45

KCl crystallizes in the same type of lattice as does NaCl. Given that

$$\frac{r_{\text{Na}^{\oplus}}}{r_{\text{Cl}^{\ominus}}} = 0.5 \text{ and } \frac{r_{\text{Na}^{\oplus}}}{r_{\text{K}^{\oplus}}} = 0.7$$

Calculate (a) the ratio of side of the unit cell for KCl to that for NaCl, and (b) the ratio of density of NaCl to that of KCl.

Sol. NaCl crystallizes in the face-centred cubic unit cell, such that

$$r_{\text{Na}^{\oplus}} + r_{\text{Cl}^{\ominus}} = a/2$$

where a is the edge length of unit cell. Now since $r_{\text{Na}^{\oplus}}/r_{\text{Cl}^{\ominus}} = 0.5$ and $r_{\text{Na}^{\oplus}}/r_{\text{K}^{\oplus}} = 0.7$, we will have

$$\frac{r_{\text{Na}^{\oplus}} + r_{\text{Cl}^{\ominus}}}{r_{\text{Cl}^{\ominus}}} = 1.5 \quad \left[\frac{r_{\text{Na}^{\oplus}}}{r_{\text{Cl}^{\ominus}}} + 1 = 0.5 + 1 \right]$$

$$\text{and } \frac{r_{\text{K}^{\oplus}}}{r_{\text{Cl}^{\ominus}}} = \frac{r_{\text{K}^{\oplus}}}{r_{\text{Na}^{\oplus}}/0.5} = \frac{0.5}{r_{\text{Na}^{\oplus}}/r_{\text{K}^{\oplus}}} = \frac{0.5}{0.7}$$

[Add 1 to both sides]

$$\text{or } \frac{r_{\text{K}^{\oplus}} + r_{\text{Cl}^{\ominus}}}{r_{\text{Na}^{\oplus}} + r_{\text{Cl}^{\ominus}}} = \frac{1.2}{0.7} \times \frac{1}{1.5}$$

$$\text{or } \frac{a_{\text{KCl}}/2}{a_{\text{NaCl}}/2} = \frac{1.2}{0.7 \times 1.5}$$

$$\text{or } \frac{a_{\text{KCl}}}{a_{\text{NaCl}}} = \frac{1.2}{1.05} = 1.143$$

$$\text{Now since } \rho = \frac{Z_{\text{eff}}}{a^3} \left(\frac{M_w}{N_A} \right)$$

$$\begin{aligned} \text{We will have } \frac{\rho_{\text{NaCl}}}{\rho_{\text{KCl}}} &= \left(\frac{a_{\text{KCl}}}{a_{\text{NaCl}}} \right)^3 \frac{M_w(\text{NaCl})}{M_w(\text{KCl})} \\ &= (1.143)^3 \left(\frac{58.5}{74.5} \right) = 1.172 \end{aligned}$$

ILLUSTRATION 1.46

LiI occurs as cubical closed packing. If the edge length of unit cell is 624 pm, determine the ionic radii of $\text{Li}^{\oplus}$ and $\text{I}^{\ominus}$ ions.

Sol. The cubical closed packing has a face-centred cubic unit cell. $\text{I}^{\ominus}$ ions occupy the corners and the face centres. These ions touch each other along the face diagonal of the cube. Hence

$$4r_{\text{I}^{\ominus}} = \sqrt{2} a$$

$$r_{\text{I}^{\ominus}} = \frac{a}{2\sqrt{2}} = \frac{624 \text{ pm}}{2(1.414)} = 220.65 \text{ pm}$$

Now along the edge, we will have $\text{I}^{\ominus}$ in $\text{Li}^{\oplus} \text{I}^{\ominus}$ arrangement, where $\text{I}^{\ominus}$ ions are at the corners and $\text{Li}^{\oplus}$ ions at the centre of the edge (octahedral void). Since in closest packing, they touch each other, we will have

$$2r_{\text{I}^{\ominus}} + 2r_{\text{Li}^{\oplus}} = a$$

$$\text{or } r_{\text{Li}^{\oplus}} = \frac{a}{2} - r_{\text{I}^{\ominus}} = \frac{624 \text{ pm}}{2} - 220.65 \text{ pm} = 91.35 \text{ pm}$$

ILLUSTRATION 1.47

The composition of a sample of Wustite is $\text{Fe}_{0.93}\text{O}_{1.00}$. What percentage of the iron is present in the form of Fe (III)?

Sol. First method

Oxidation number (ON) of Fe in $\text{Fe}_{0.93}\text{O}$

$$= 0.93 \times X - 2 \times 1 = 0 \Rightarrow X = 2.15$$

Oxidation number (ON) of Fe is an intermediate value of Fe^{2+} and Fe^{3+}

Let % of $\text{Fe}^{3+} = a$

$$\frac{3 \times a + 2(100 - a)}{100} = 2.15 \Rightarrow a = 15.05\%$$

$$\therefore \text{Percent of } \text{Fe}^{3+} = 15.05 \quad \% \text{ of } \text{Fe}^{2+} = 84.95$$

Second method

Let X atoms of Fe^{3+} ions are present in the compounds.

$$\therefore \text{Fe}_{0.93} (\text{Number of } \text{Fe}^{3+} \text{ ions} + \text{Number of } \text{Fe}^{2+} \text{ ions})$$

$$\begin{aligned} \text{Number of } \text{Fe}^{2+} \text{ ions} &= \text{Total} - \text{Number of } \text{Fe}^{3+} \\ &= (0.93 - X) \end{aligned}$$

Total positive charge (i.e., on $\text{Fe}^{2+} + \text{Fe}^{3+}$) = Total (negative) charge on oxygen

$$2(0.93 - X) + 3X = 2 \Rightarrow X = 0.14$$

$$\therefore \text{Percent of } \text{Fe}^{3+} = 0.14/0.93 \times 100 = 15.05$$

ILLUSTRATION 1.48

CsBr crystallizes in a body-centred cubic unit lattice with an edge length of 4.287 Å. Calculate the angles at which the second-order reflection maxima may be expected for (2, 0, 0), (1, 1, 0), and (1, 1, 1) planes when X-rays of $\lambda = 0.50$ Å are used.

Sol. For bcc lattice, $d_{200} = a/2$

$$\text{So, for second-order reflection, } 2\lambda = 2 \times \frac{a}{2} \sin \theta_1$$

$$\text{or } \sin \theta_1 = \frac{2\lambda}{a}$$

$$\text{i.e., } \sin \theta_1 = \frac{2 \times 0.50}{4.287} \text{ and } \theta_1 = 13^\circ 29'$$

$$d_{110} = \frac{a}{\sqrt{2}}$$

$$\text{So, } 2\lambda = 2 \times \frac{a}{\sqrt{2}} \sin \theta_2 \Rightarrow \sin \theta_2 = \frac{\sqrt{2}\lambda}{a}$$

$$\sin \theta_2 = \frac{\sqrt{2} \times 0.50}{4.284} \Rightarrow \theta_2 = 9^\circ 30'$$

$$d_{111} = \frac{a}{2\sqrt{3}}, \text{ so } 2\lambda = 2 \times \frac{a}{2\sqrt{3}} \sin \theta_3 \Rightarrow \sin \theta_3 = \frac{2\sqrt{3}\lambda}{a}$$

$$\text{i.e., } \sin \theta_3 = \frac{2 \times \sqrt{3} \times 0.50}{4.287} \text{ and } \theta_3 = 23^\circ 49'$$

1.24 HAUY'S LAW OF RATIONAL INDICES

Haüy's law states that the intercepts of any face of a crystal along the crystallographic axes are either equal to the unit intercepts (a , b , c) or some simple whole number multiples of them, e.g., na , $n'b$, $n''c$, etc., where, n , n' , n'' , etc., are simple whole numbers. Let OX, OY, and OZ represent the three crystallographic axes and let ABC be a unit plane.

The unit intercepts will then be a , b , and c (Fig. 1.67).

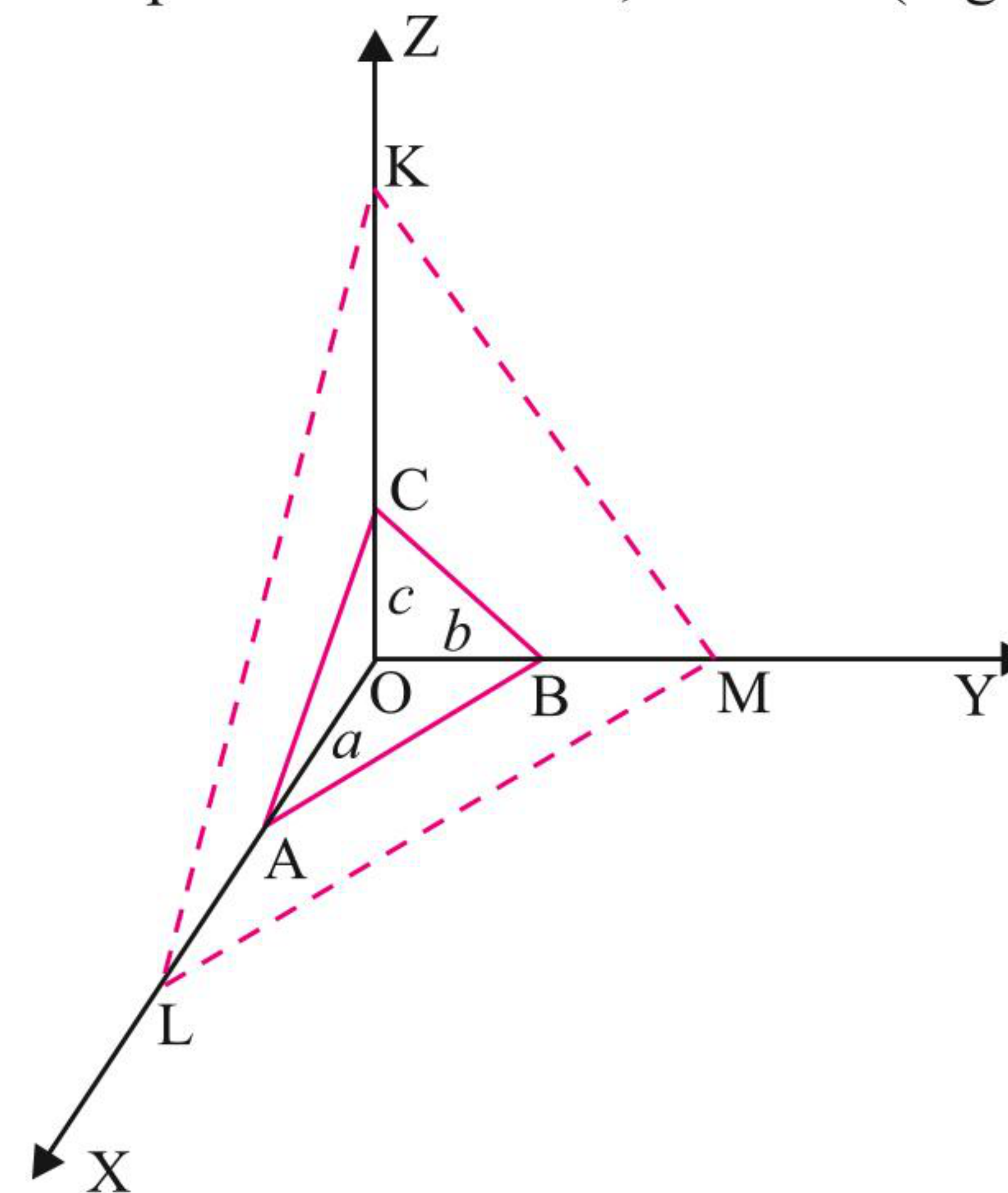


Fig. 1.67 Intercept of crystallographic plane

According to the above law, the intercept of any faces such as KLM, on the same three axes will be simple whole number multiples of a , b , and c , respectively. As can be seen from the figure, the simple multiples of this case are 2, 2, and 3.

1.24.1 WEISS INDICES

The coefficients a , b , c , i.e., l , m , n are known as weiss indices of a plane. For example, for a crystal plane which cut through the crystal axes at $(2a, 3b, c)$, the weiss indices are 2, 3, 1.

1.24.2 MILLER INDICES

Miller indices are a set of integers (h, k, l) which are used to describe a given plane in a crystal. The miller indices of a face of a crystal are inversely proportional to the intercepts of that face on various axes.

Reciprocal of the weiss coefficients and multiplying through by the smallest number will express all the reciprocals as integers.

The actual lattice in a crystal of a given kind consists of a repetition of a unit cell of that kind all over in three-dimensional space. As already mentioned, there can only be a maximum of 32 elements of symmetry (point groups). Combining these with 14 Bravais lattices there can be 230 different arrangements known as space groups.

ILLUSTRATION 1.49

Calculate the miller indices of crystal planes which cut through the crystal axes at

- | | |
|---------------------|----------------------|
| i. $(2a, 3b, c)$ | ii. (a, b, c) |
| iii. $(6a, 3b, 3c)$ | iv. $(2a, -3b, -3c)$ |

Sol. Following the procedure given above, we prepare the tables as follows:

i.	a	b	c	ii.	a	b	c
	2	3	1		1	1	1
	1/2	1/3	1		1	1	1
	3	2	6		1	1	1

Hence, the miller indices are (326).

iii.	a	b	c	iv.	a	b	c
	6	3	3		2	-3	-3
	1/6	1/3	1/3		1/2	-1/3	-1/3
	1	2	2		3	-2	-2

Hence, the miller indices are (122).

Hence, the miller indices are $(\bar{3}\bar{2}\bar{2})$.

1.24.3 d-SPACINGS

The distance between two parallel planes in a cubic crystal (d -spacing) is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a is the length of the side of the cube and h , k , and l are miller indices of the parallel planes.

For the planes (100), (110), and (111) in a cubic unit cell,

a. sc [Fig. 1.68(a)]

$$d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a$$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

$$\frac{1}{d_{100}} : \frac{1}{d_{110}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \sqrt{3}$$

$$d_{100} : d_{110} : d_{111} = 1 : 0.71 : 0.58$$

b. fcc [Fig 1.68(b)]

$$\begin{aligned} d_{200} : d_{220} : d_{111} &= \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{\sqrt{3}} \\ &= \frac{1}{2} : \frac{1}{2\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : \frac{1}{\sqrt{2}} : \frac{2}{\sqrt{3}} \\ &= 1 : 0.707 : 1.154 \end{aligned}$$

$$\frac{1}{d_{200}} : \frac{1}{d_{220}} : \frac{1}{d_{111}} = 1 : \sqrt{2} : \frac{\sqrt{3}}{2}$$

c. bcc [Fig. 1.68(c)]

$$\begin{aligned} d_{200} : d_{110} : d_{222} &= \frac{a}{2} : \frac{a}{\sqrt{2}} : \frac{a}{2\sqrt{3}} \\ &= \frac{1}{2} : \frac{1}{\sqrt{2}} : \frac{1}{2\sqrt{3}} \\ &= 1 : 1.404 : 0.577 \end{aligned}$$

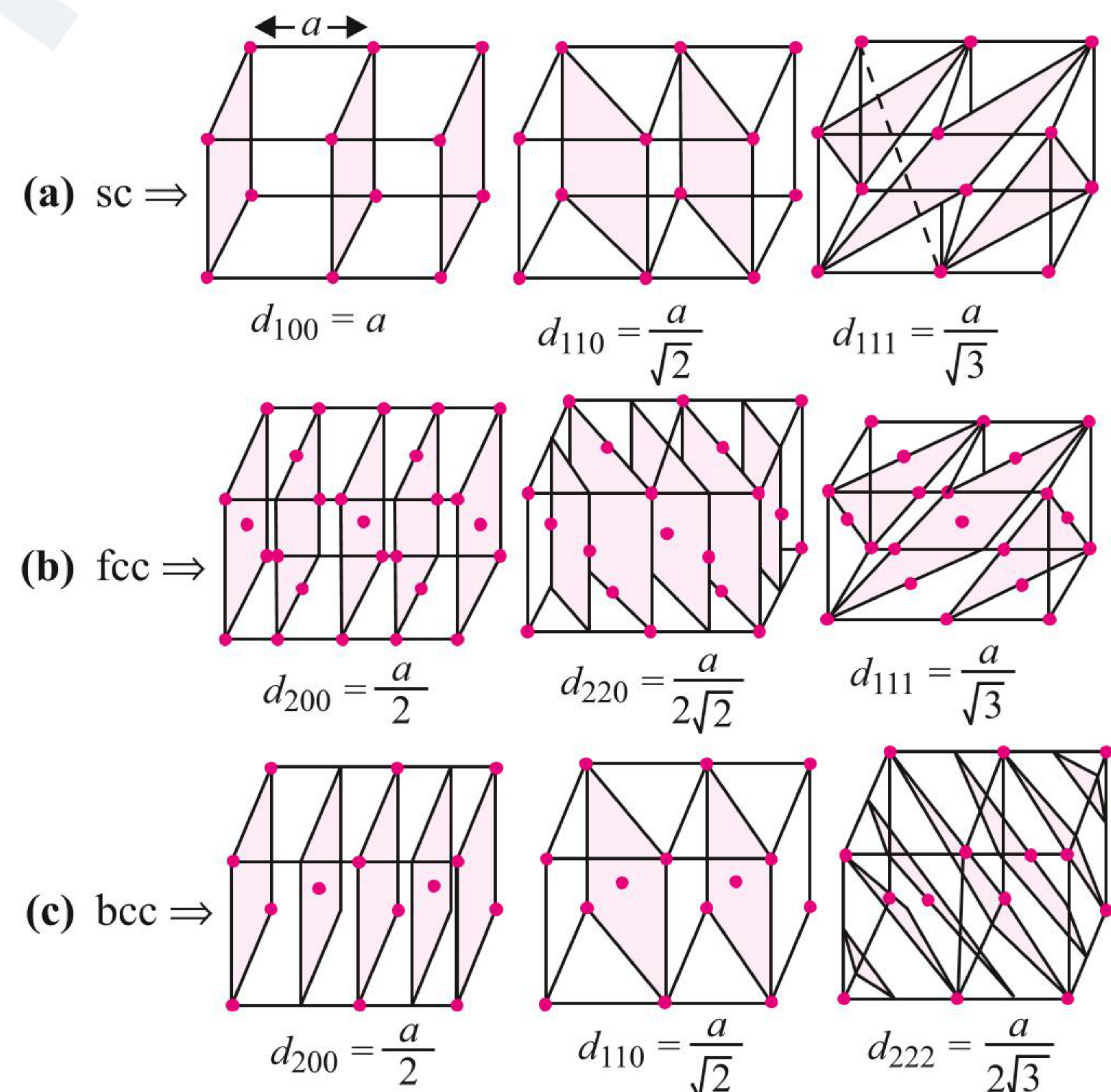


Fig. 1.68 Lattice plane separations for the cubic systems

1.24.4 INTERPLANAR DISTANCES FOR CUBIC SYSTEM

- (100) planes: Distance between these planes is equal to the length a of the side of cube, i.e., $d_{100} = a$.
- (200) planes: Distance between these planes is equal to the half length $a/2$ of the side of a cube, i.e., $d_{200} = a/2$.
- (110) planes: Spacing between these planes is one-half of the diagonal of the square base of the cube, i.e.,

$$d_{100} = (\sqrt{a^2 + a^2}) / 2 = a / \sqrt{2}.$$

- d. (111) planes: The entire cross diagonal d of a cube spans three (111) planes. Thus, the distance between the two of each of these planes is $d/3$. Now,

$$d = \sqrt{a^2 + a^2 + a^2} = \sqrt{3} a$$

$$\therefore d_{111} = \frac{\sqrt{3} a}{3} = \frac{a}{\sqrt{3}}$$

- e. (222) planes: These planes are in between (111) planes. Thus, the distance between any two such planes is

$$d_{222} = \frac{d_{111}}{2} = \frac{a}{2\sqrt{3}}$$

ILLUSTRATION 1.50

How do the spacings of the three planes 100, 110, and 111 of cubic lattice vary?

Sol. Applying the formula $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

$$d_{100} = \frac{a}{\sqrt{1^2 + 0^2 + 0^2}} = a$$

$$d_{110} = \frac{a}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{a}{\sqrt{2}}$$

$$d_{111} = \frac{a}{\sqrt{1^2 + 1^2 + 1^2}} = \frac{a}{\sqrt{3}}$$

$$\text{Thus, } d_{100} : d_{110} : d_{111} = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} = 1 : 0.707 : 0.577$$

ILLUSTRATION 1.51

Potassium chloride crystallize with a body-centred cubic lattice. Calculate the distance between the 200, 110, and 222 planes. The length of the side of the unit cell is 5.34 Å.

Sol. $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

$$\text{For 200 plane } d_{200} = \frac{5.34}{\sqrt{2^2 + 0^2 + 0^2}} = \frac{5.34}{\sqrt{4}} = 2.67 \text{ Å}$$

$$\text{For 110 plane, } d_{110} = \frac{5.34}{\sqrt{1^2 + 1^2 + 0^2}} = \frac{5.34}{\sqrt{2}} = 3.77 \text{ Å}$$

$$\text{For 222 plane, } d_{222} = \frac{5.34}{\sqrt{2^2 + 2^2 + 2^2}} = \frac{5.34}{\sqrt{12}} = 1.54 \text{ Å}$$

ILLUSTRATION 1.52

Diamond has face-centred cubic lattice. There are two atoms at $(0, 0, 0)$ and $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ coordinates. The ratio of the carbon-carbon bond distance to the edge of the unit cell is

- a. $\sqrt{\frac{3}{16}}$ b. $\sqrt{\frac{1}{4}}$ c. $\frac{1}{4}$ d. $\frac{1}{\sqrt{2}}$

Sol. a. Distance between $(0, 0, 0)$ and $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right) = 2r$

$$\Rightarrow 2r = \frac{\sqrt{3}a}{4}$$

$$\Rightarrow \frac{2r}{a} = \sqrt{\frac{3}{16}}, \text{ where } 2r = \text{bond distance}$$

ILLUSTRATION 1.53

Which of the following statements is(are) correct for the diamond structure?

- Each atom has 4 nearest neighbours and 12 next nearest neighbours.
- It is relatively empty.
- The maximum proportion of the available volume which may be filled by hard spheres is only 0.34.
- The maximum proportion of the available volume which may be filled by hard spheres is only 0.46.

Sol. (a, b, c)

Atom (carbon) lying in the tetrahedral voids touches the surrounding 4 atoms at a distance of $\sqrt{3}a/4$, and the face centre atom has 12 next nearest neighbours at a distance of $a/\sqrt{2}$.

For PF, refer section 1.17.

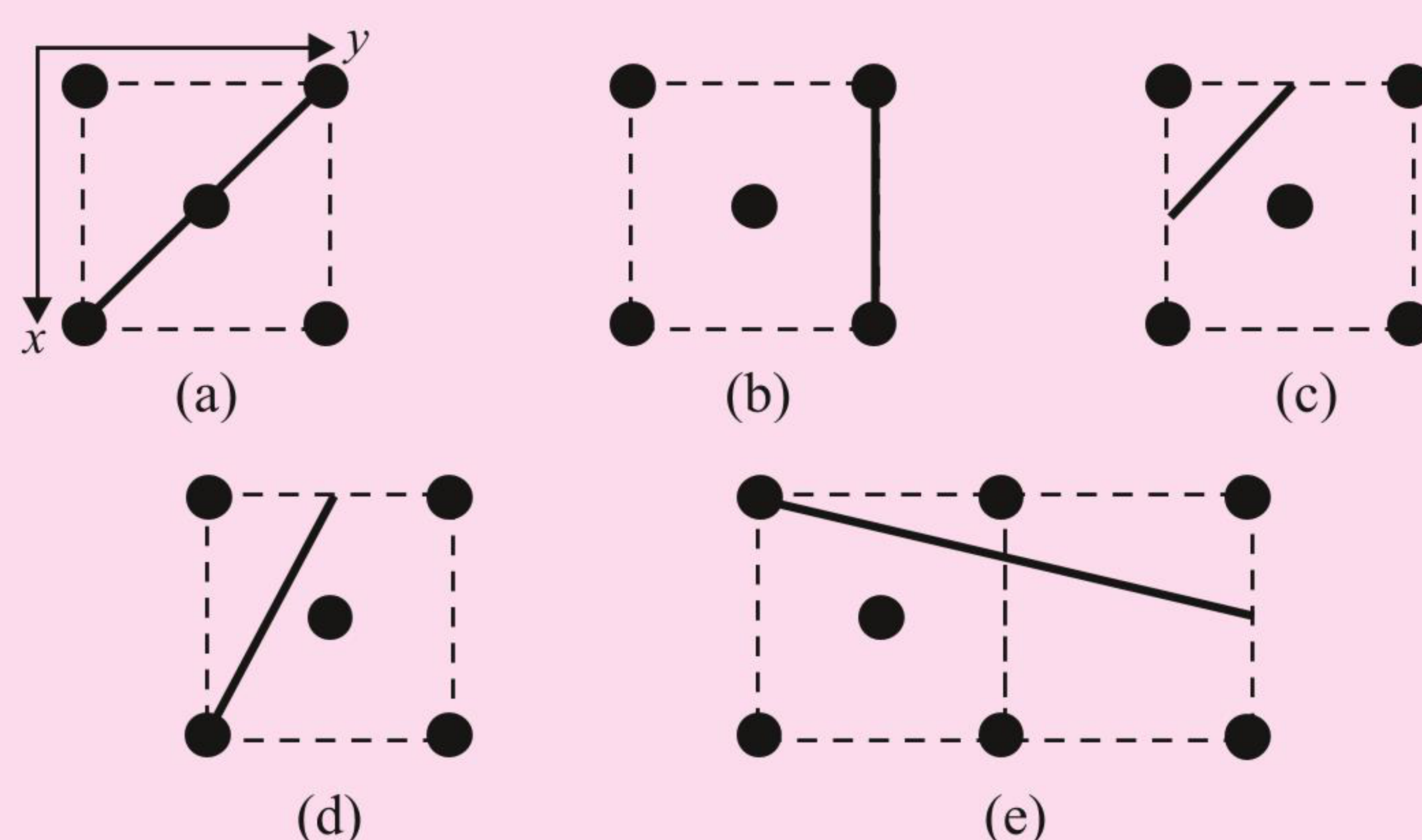
$$\text{The packing fraction (PF)} = \frac{8 \times \frac{4}{3} \pi R^3}{a^3}$$

$$\text{where } 2R = \frac{\sqrt{3}a}{4} \Rightarrow \frac{R}{a} = \frac{\sqrt{3}}{8}$$

$$\text{Hence, PF is: } \frac{32}{3} \pi \left(\frac{3\sqrt{3}}{8 \times 64} \right) = \frac{\sqrt{3}\pi}{16} \approx 0.34$$

ILLUSTRATION 1.54

Consider the two-dimensional “unit cell” shown in figure (a)–(e) below.



- i. What are the miller indices of the line shown in Fig. (a)?

- a. 1, 1 b. 1, 0 c. 0, 1 d. 2, 2

- ii. What are the miller indices of the line shown in Fig. (b)?
 a. 1, 1 b. 1, 0 c. 0, 1 d. 2, 2
- iii. What are the miller indices of the line shown in Fig. (c)?
 a. 1, 1 b. 1, 0 c. 0, 1 d. 2, 2
- iv. Which of the following sketches shows the 12 line in a two-dimensional unit cell?
 a. Fig. a b. Fig. c c. Fig. d d. Fig. e
- v. Which of the following sketches shows the $(2, \bar{1})$ line in a two-dimensional unit cell?
 a. All figures b. Fig. d c. Fig. e d. None

Sol. i. a. The miller indices are a set of integers hkl that are used to describe a given plane in a crystal. For this two-dimensional plane, only hk will be used. The procedure for determining the Miller indices for a plane is:

- (I) Prepare a table with the unit cell axes at the top of columns.
- (II) Enter in each column the intercept (expressed as a multiple of a , b or c) of the plane with that axis.
- (III) Invert all numbers
- (IV) Clear fractions to obtain h , k , and l .

Table for Fig. (a)

a	b	
1	1	Intercepts
1	1	Reciprocals
1	1	Clear fraction

$\therefore$ Miller indices as 1, 1.

ii. c. Table for Fig. (b)

a	b	
∞	1	Intercepts
0	1	Reciprocals
0	1	Clear fractions

$\therefore$ Miller indices as 0, 1.

iii. d. Table for Fig. (c)

a	b	
1/2	1/2	Intercepts
2	2	Reciprocals
2	2	Clear fractions

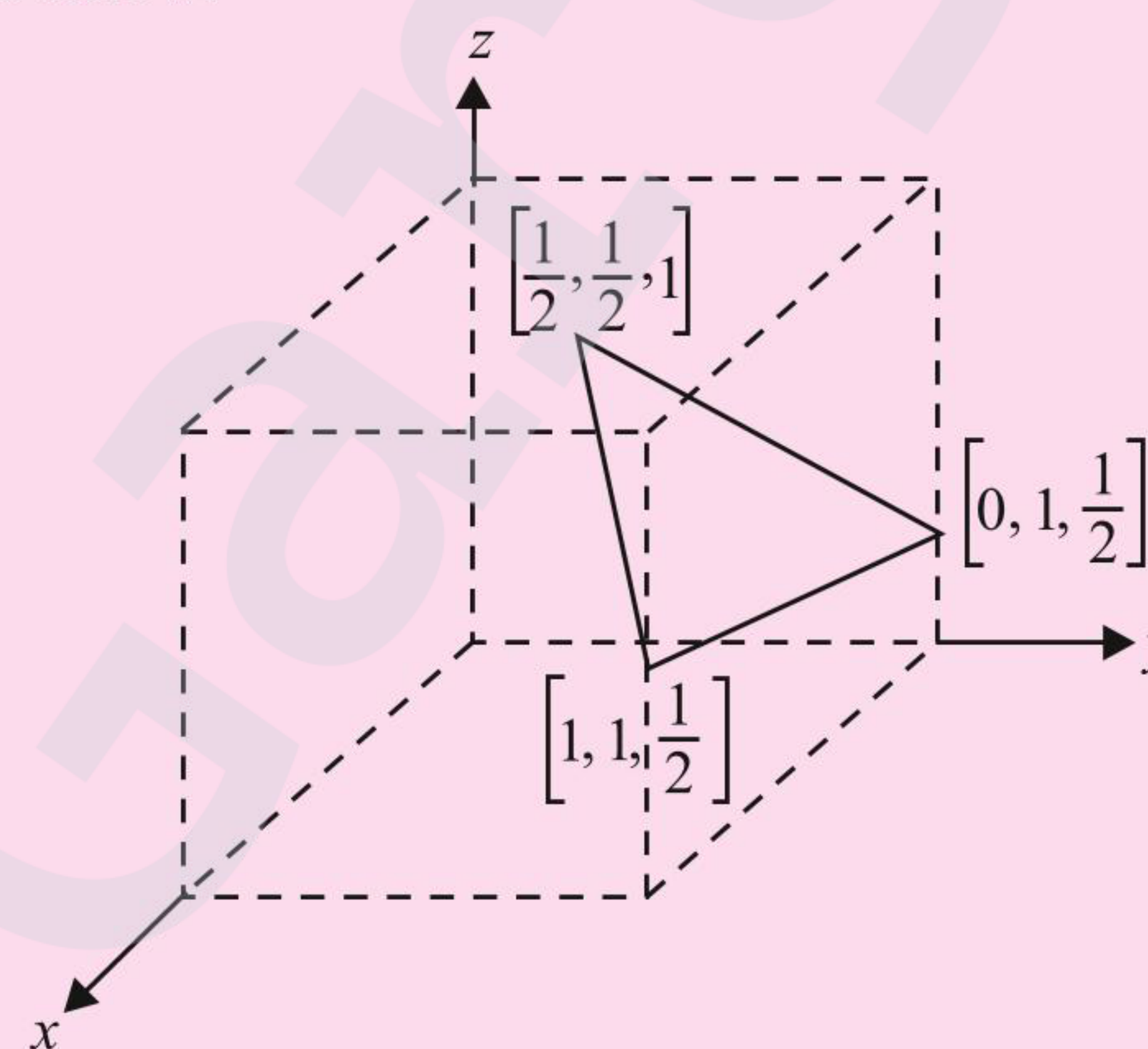
$\therefore$ Miller indices as 2, 2.

- iv. c. The miller indices represent the number of equal segments into which each respective axis has been divided by the plane. For the 12th line, the a -axis has been intersected at unity and the b -axis has been intersected into two equal segments. The line from $x = \frac{a}{1}$ to $y = \frac{b}{2}$, shown in Fig. (d), is the 12th line.

- v. c. The bar over 1 in the set of indices represents -1 . The $\bar{2}$ line divides the a axis into two equal segments and intersects the b axis at $-b$. The line from $x = a/2$ to $y = -b/1$ is shown in Fig. (e).

ILLUSTRATION 1.55

The coordinates of three corners of an octahedral face on a cubic unit cell are $(\frac{1}{2}, \frac{1}{2}, 1)$, $(0, 1, \frac{1}{2})$ and $(1, 1, \frac{1}{2})$ as shown in the figure below.



The miller indices of this plane is

- a. 0, 1, 1 b. 1, 0, 1 c. 0, 0, 1 d. 1, 1, 1

Sol. a. The plane is shown in the figure above. The intercepts with the axes are ∞ , $2b$, and $2c$.

Table for the figure shown above:

a	b	c	
∞	2	2	Intercepts
0	1/2	1/2	Reciprocals
0	1	1	Clear fractions

$\therefore$ Miller indices are 0, 1, 1.

CONCEPT APPLICATION EXERCISE 1.1

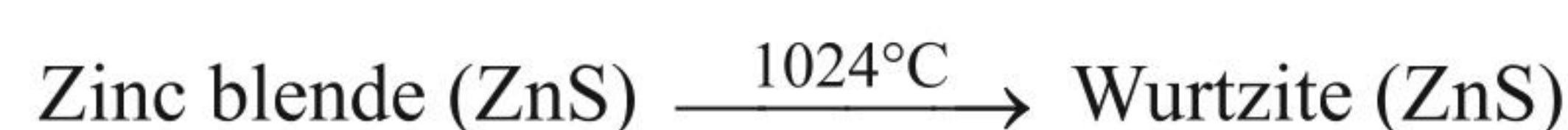
1. A compound formed by elements X and Y crystallizes in the cubic structure when Y atoms are at the corners of the cube and X atoms are at the alternate faces. What is the formula of the compound?
2. Calculate the number of atoms in a cubic-based unit cell having one atom on each corner and two atoms one each diagonal.
3. A compound made up of elements A and B crystallizes in the cubic structures. Atoms A are present on the corners as well as face centres whereas atoms B are present on the edge centres as well as body centre. What is the formula of the compound? Draw the structure of its unit cell.
4. In an fcc arrangement of A and B atoms whose A atoms are at the corners of the unit cell and B atoms are at the face centres, one of the A atom is missing from one corner in each unit cell. What is the simplest formula of the compound?

-

- The coordinates of TVs nearest and farthest to the origin.
- The distance between two successive TVs
- The coordinates of OVs nearest and farthest to the origin
- The distance between two successive OVs.

1. XY 2. $Z_{\text{eff}} = 9$ 3. AB 4. A_7B_{24} 5. 241 pm
6. A_2B 7. Al_2O_3 8. (a) 387 pm (b) 335.1 pm (c) 154.1 pm
9. 123.3 to 217.4 pm 10. No 11. AB_2O_4
12. (a) i. CN of $Mg^{2+} = 6$ ii. CN of $Tl^{\oplus} = 8$
CN of $O^{2-} = 6$ CN of $Cl^{\ominus} = 8$
(b) 100 pm (min), 176.81 pm (max) (c) OV's (d) 346.4 pm
13. (a) 5% (b) 8.21 g cm^{-3} (c) 8.26 g cm^{-3}
14. (a) TV nearest = $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ (b) TV farthest = $\left(\frac{39}{4}, \frac{39}{4}, \frac{39}{4}\right)$
(c) OV nearest = $\left(0, \frac{a}{2}, 0\right); \left(\frac{a}{2}, 0, 0\right); \left(0, 0, \frac{a}{2}\right)$
(d) OV farthest = $\left(\frac{a}{2}, a, a\right); \left(a, \frac{a}{2}, a\right); \left(a, a, \frac{a}{2}\right)$

Many solids exist only in one single crystalline form. However, many solids occur in more than one modification. For example, sodium chloride crystallizes as cubes. It can also be made to crystallize as octahedra. This occurrence of different crystal forms of the same substance is called polymorphism. Sodium chloride crystallizes as octahedra from an aqueous solution containing 15% urea. Interconversions of polymorphs take place at a given temperature. This is the transition temperature at the specified pressure at which the transition is studied. Some transitions are reversible, some are not.



Polymorphism occurring in elements is commonly termed as *allotropy*. Three types of allotropy are distinguished depending on the method of transition from one to another: enantiotropy, monotropy, and dynamic allotropy.

If one modification is interconvertible to another at a fixed temperature (transition temperature) under a specified pressure, then this type of allotropy is termed as *enantiotropy*. The system rhombic and monoclinic sulphur exemplify this case. At 96.6°C, rhombic sulphur is converted to monoclinic and vice versa. Above 96.6°C, monoclinic sulphur is stable and below 96.6°C rhombic sulphur is stable.

Monotropic systems are systems where one modification is unstable at all temperatures and is converted to the stable form. Ozone–oxygen, red phosphorus–yellow phosphorus are such cases.

In *dynamic allotropy*, both forms exist side by side in equilibrium at all temperatures. A typical example of this case is λ - and μ -sulphur. The proportion of the two forms at equilibrium depends on temperature.

1.25.1 ISOMORPHISM AND ISOPOLYMORPHISM

Many pairs of compounds of similar composition are found to crystallize in the same form. Some common examples are:

- $\text{KH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{KH}_2\text{AsO}_4 \cdot \text{H}_2\text{O}$
- K_2SO_4 and K_2SeO_4
- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSeO}_4 \cdot 5\text{H}_2\text{O}$
- $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ and $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

The word “isomorphous” is applied to these substances. This may be stated as an equal number of atoms combined in the same way produce the same crystalline form. The crystalline form is independent of the chemical nature of the combined atoms.

Isomorphism can be detected by the following criteria:

- Similarity of crystalline form
- Formation of mixed crystals
- Formation of overgrowth

In case of polymorphic substances, if each of the two different forms of a polymorphic substance is isomorphous with a form of another polymorphic substance, then the phenomenon is termed as *isopolymorphism*.

Law of isomorphism

An isomorphous substance forms crystals which have the same shape and can grow in the saturated solution of each other. According to Mitscherlich, isomorphous substances have similar chemical constitution, i.e., they have the same number of atoms similarly arranged. Their formulae are, therefore, similar, for example, K_2SO_4 and K_2CrO_4 are isomorphous and so are $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

MnSO_4 shows three types of hydrated salts.

	Salt	Temp. of crystallization	Crystalline form
a.	$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$	Below 273 K	Rhombic like vitriol
b.	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$	273–298 K	Asymmetric and isomorphous with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
c.	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	Above 298 K	Monosymmetric prism

ILLUSTRATION 1.56

Which of the following compounds are not isomorphous?

- Copper sulphate and zinc sulphate
- Zinc sulphate and manganese sulphate
- Calcium carbonate and ferrous sulphate
- Zinc sulphate and ferrous sulphate

Sol.

- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ are not isomorphous. Different moles of H_2O .
- $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ are isomorphous, with 7 H_2O in both compounds.
- CaCO_3 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are not isomorphous, since the moles of H_2O are not same.
- $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ are isomorphous with same number of moles of H_2O .

ILLUSTRATION 1.57

Potassium selenate is isomorphous with potassium sulphate and contains 50.0% of Se. The atomic weight of Se is

- 142
- 71
- 47.33
- 284

Sol.

- K_2SO_4 and potassium selenate are isomorphous. So the formula is K_2SeO_4 .

$$M_w \text{ of } \text{K}_2\text{SeO}_4 = (39 \times 2 + x + 64) \\ = (142 + x)\text{g}$$

$$\therefore (142 + x) \text{ of } \text{K}_2\text{SeO}_4 \Rightarrow x \text{ g of Se}$$

$$100 \text{ g of } \text{K}_2\text{SeO}_4 = \frac{x}{(142 + x)} \times 100$$

$$\therefore \frac{x \times 100}{(142 + x)} = 50$$

ILLUSTRATION 1.58

The *Ew* of an element is 13. It forms an acidic oxide which with KOH forms a salt isomorphous with K_2SO_4 . The *Aw* of element is

- 13
- 26
- 52
- 78

Sol. d. MSO_4 and K_2SO_4 are isomorphous.

Thus, valency of S and M should be same = 6.

$$\therefore A_w = E_w \times \text{Valency} \\ = 13 \times 6 = 78.$$

1.26 IMPERFECTIONS IN SOLIDS

According to the Nernst law (third law of thermodynamics), true crystals possess perfect order of arrangement of atoms only at 0 K. But some deviation from complete order takes place with the increase in temperature. The presence of impurities also adds to imperfections in solids. These imperfections modify and impart new properties to the crystal.

Any departure from perfectly ordered arrangement of atoms/ions in a crystal is called imperfection or crystal defect.

There are three types of imperfections:

- a. Electronic imperfections
- b. Atomic or point defects
- c. Line defects or dislocations

1.26.1 ELECTRONIC IMPERFECTIONS

Electrons in ionic (e.g., NaCl) or covalent (e.g., Si) crystals occupy the lowest energy level at 0 K (absolute zero). Above 0 K, in pure Si or Ge, electrons are released from the covalent bonds. It leads to the presence of free electrons and electron-deficient bonds called holes, which are responsible for intrinsic conduction. These free electrons and holes in crystals are responsible for electronic imperfections.

Note:

- a. The following new terms will be used in this section:
 - i. Intrinsic conduction: Conduction which is caused in a crystal due to heating, leading to the formation of free electrons and holes, e.g., crystals of Si or Ge.
 - ii. Hole: An electron-deficient bond formed by the release of an electron.
 - iii. n : Concentration of electrons (e)
 - iv. p : Concentration of holes (h).
- b. Atoms in a solid vibrate like a simple harmonic oscillator. They have different modes of vibration. When transition takes place from a higher vibrational state to a lower vibrational state, a quantum of thermal energy is emitted. This quantum number of thermal energy is called phonon in analogy to photon for light energy. Absorption of phonons by a crystal can produce atomic displacement leading to imperfection.

1.26.2 ATOMIC OR POINT DEFECTS

Crystalline solids have short-range as well as long-range order in the arrangement of their constituent particles, yet crystals are not perfect. A solid consists of an aggregate of large number of small crystals. These small crystals have defects in them. This happens when crystallization process occurs at fast or moderate rate. Single crystals are formed when the process of crystallization occurs at extremely slow rate. Even these crystals are not free of defects. The defects are basically irregularities in the arrangement of constituent particles. One such defect is point defect. Point defects are irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. Point defects are classified into three types: (a) stoichiometric defects, (b) non-stoichiometric defects, and (c) impurity defects.

Stoichiometric Defects

The point defects which do not disturb the stoichiometry of the solid are also called *intrinsic* or *thermodynamic defects*. Shown by non-ionic compounds, stoichiometric defects are of two types: vacancy defects and interstitial defects.

Vacancy defect

When some of the lattice sites are vacant, the crystal is said to have vacancy defect (Fig. 1.69). This results in a decrease in the

density of the substance. This defect can also develop when a substance is heated.

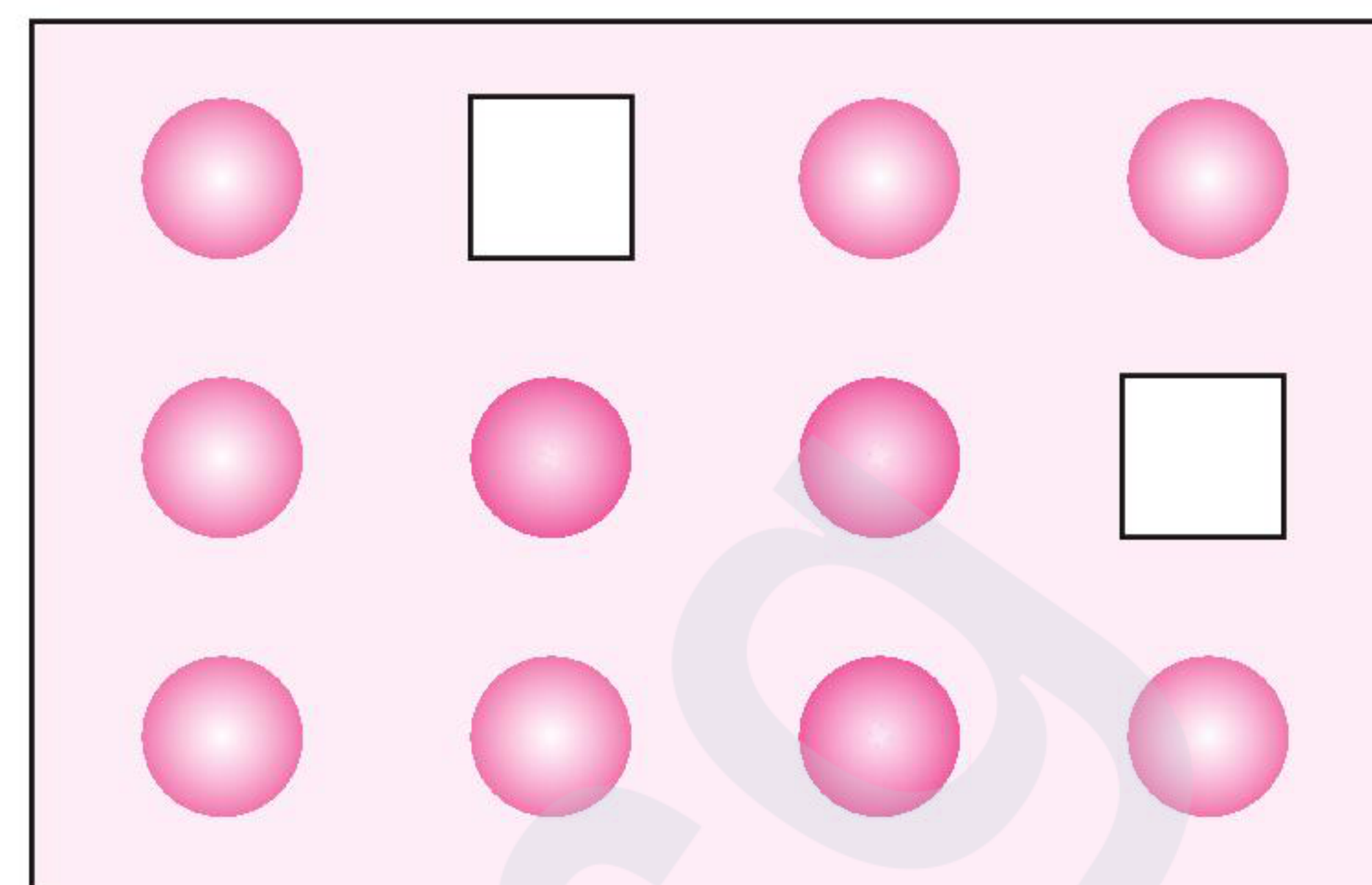


Fig. 1.69 Vacancy defects

Interstitial defect

When some constituent particles (atoms or molecules) occupy an interstitial site, the crystal is said to have interstitial defect (Fig. 1.70). This defect increases the density of the substance. An important factor in determining the formation of interstitial defect is the size of the atom (or ion) because they are accommodated into the void.

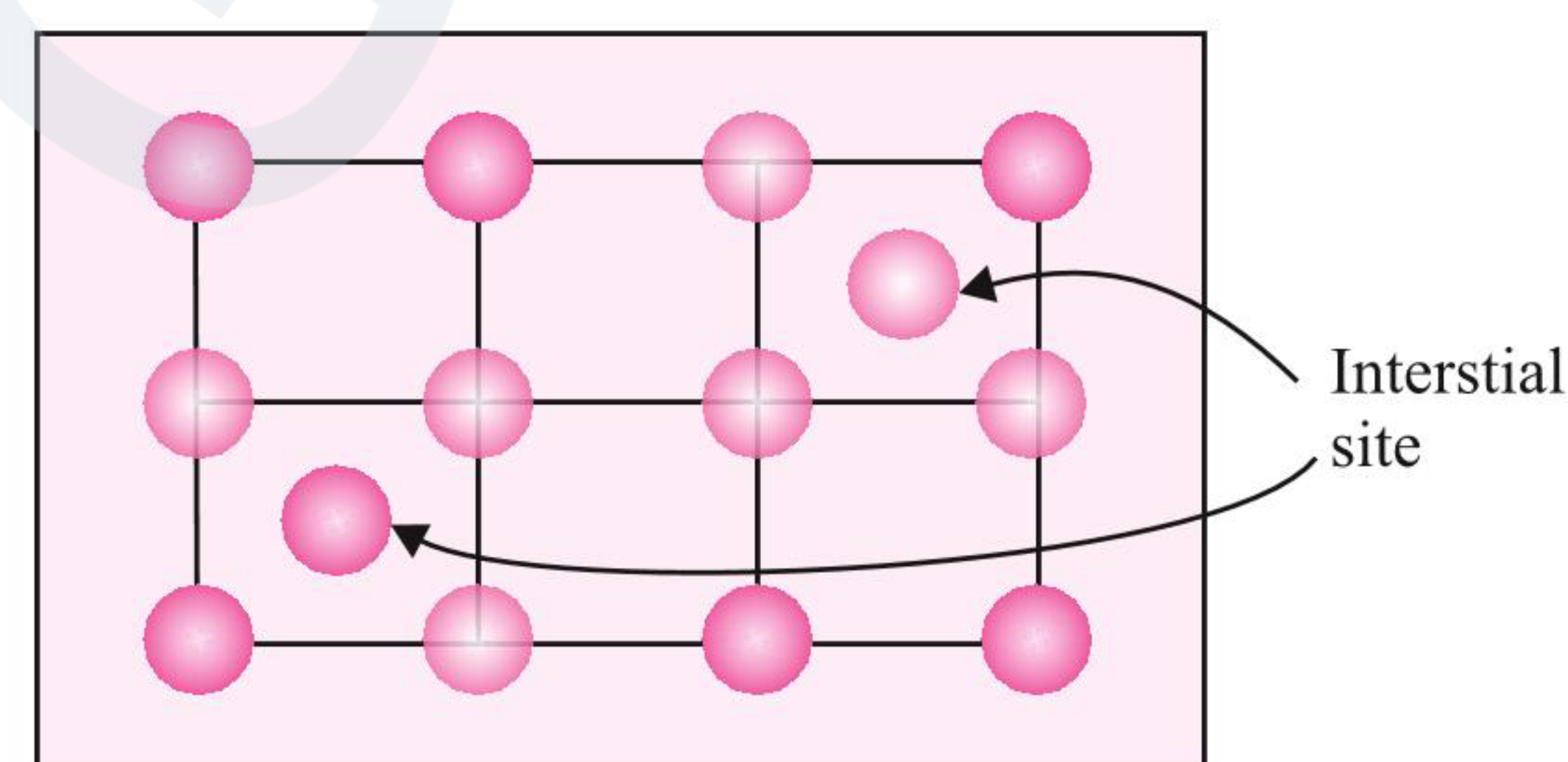


Fig. 1.70 Interstitial defects

Vacancy and interstitial defects as explained above can be shown by non-ionic solids. Ionic solids must always maintain electrical neutrality. Rather than simple vacancy or interstitial defects, they show defects such as Frenkel and Schottky defects.

Schottky defect

In ionic crystals of the type $A^+ B^-$, equal number of anions and cations are missing from the lattice sites so that electrical neutrality is maintained. This type of defect is called Schottky defect (Fig. 1.71).

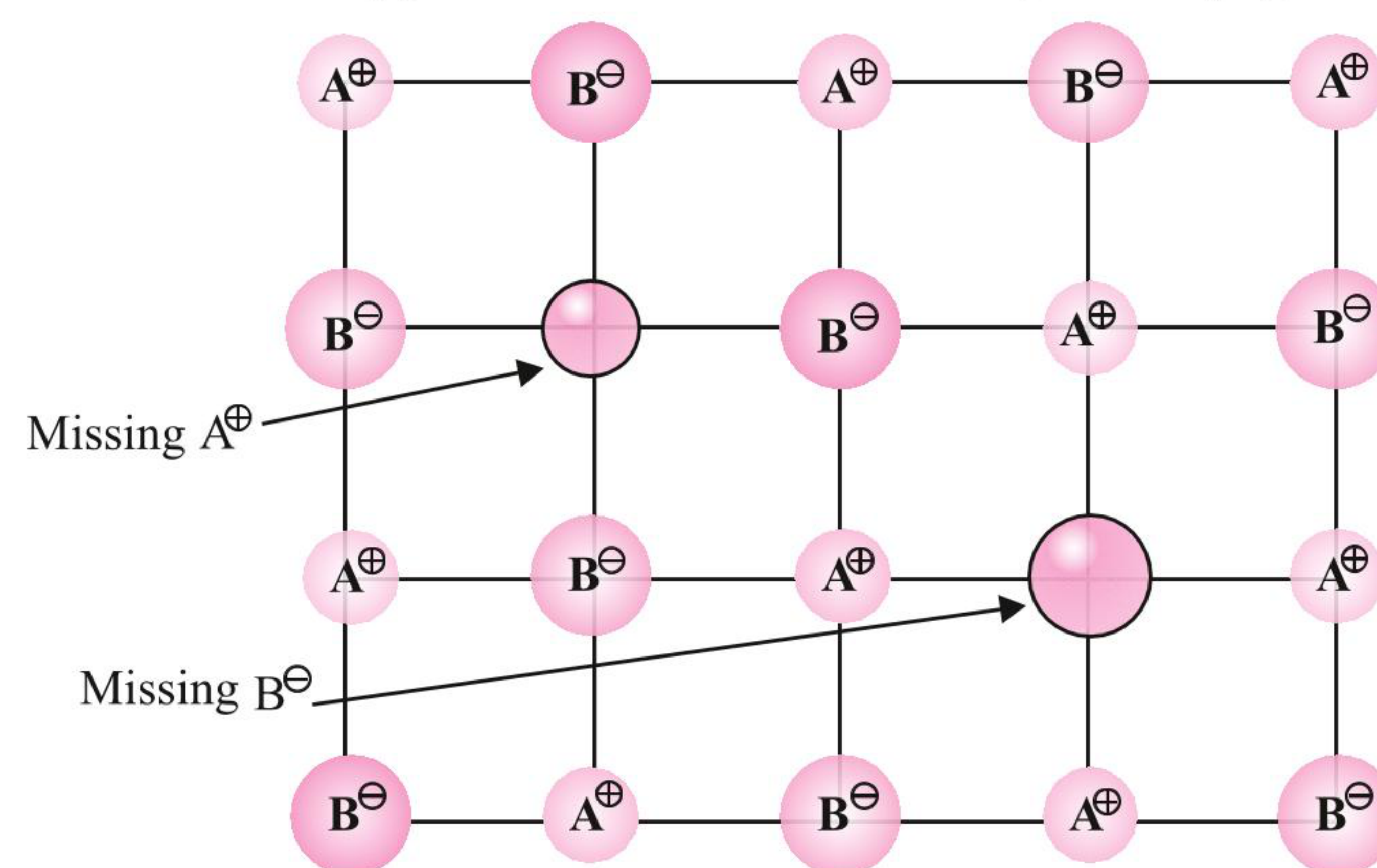


Fig. 1.71 Schottky defects

This type of defect is shown by highly ionic compounds which have high coordination number and cations and anions of similar sizes. For example, KCl, NaCl, AgBr, KBr, and CsCl.

Effects of Schottky defect

- As the number of ions decreases and volume remains same, so the density decreases.
- Crystals with Schottky defect conduct electricity to a small extent. This is because if an ion moves from its lattice site to occupy a “hole,” it creates a new “hole.” In this way, a hole moves across the crystal which as a result moves the charge in the opposite direction.
- Due to the presence of holes, the stability (or lattice energy) of the crystal decreases.

Frenkel defect

If an ion is missing from its lattice site (causing a vacancy or a hole there) and occupies an interstitial site so that the electrical neutrality as well as stoichiometry of the compound are maintained, this type of defect is called Frenkel defect (Fig. 1.72). Since the size of cations is generally smaller, it is more likely that cations occupy interstitial sites.

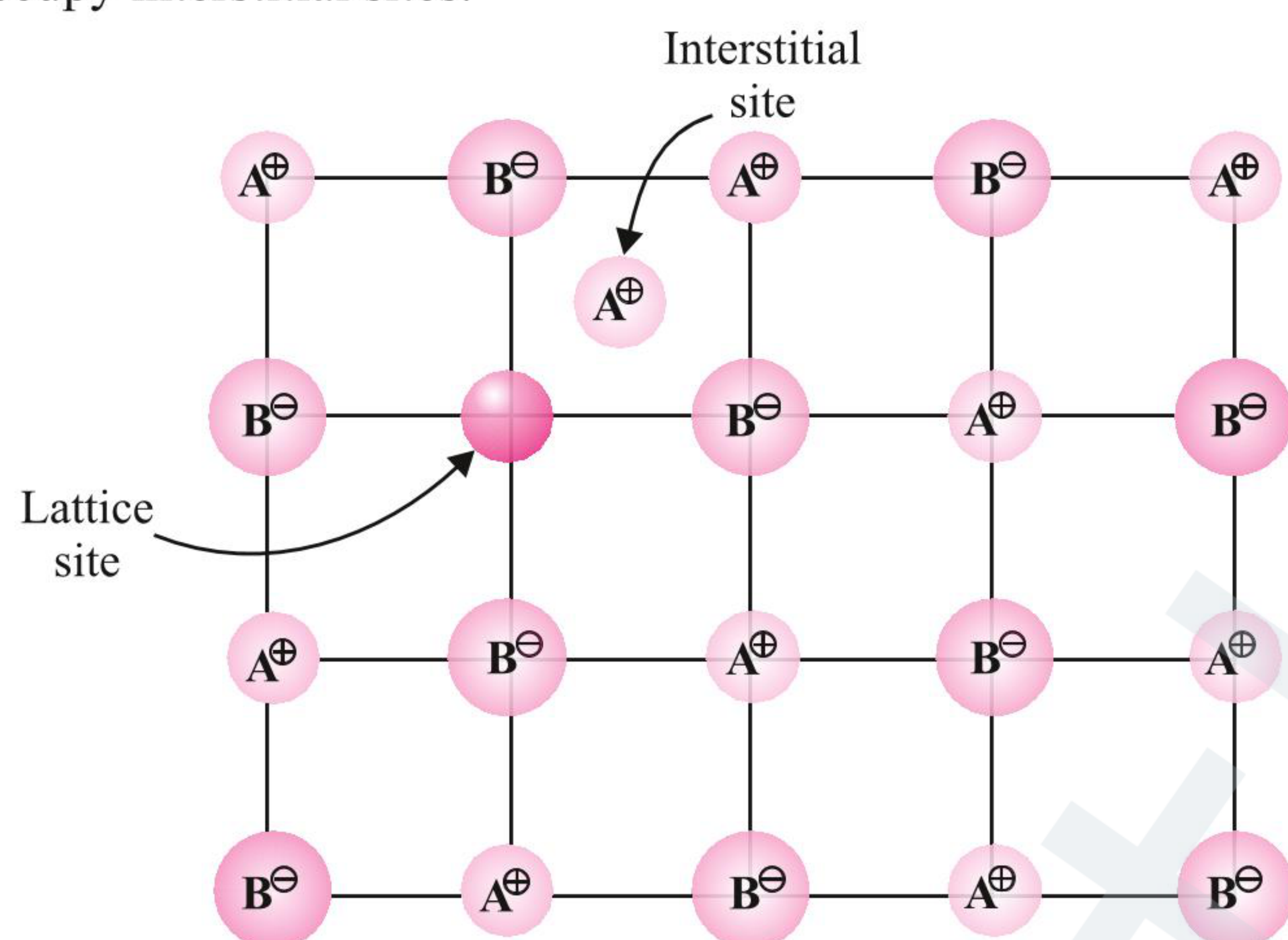


Fig. 1.72 Frenkel defect

Effects of Frenkel defect

- This type of defect is present in those compounds which have low coordination number.
- Large difference in size of anion and cation, e.g., AgCl, AgBr, AgI, and ZnS.
- Solids with this defect conduct electricity to a small extent.
- The dielectric constant of the crystal increases.
- The density of the solid is unchanged.
- Due to the presence of holes, the stability of the crystal decreases.

Note:

- The above two defects are intrinsic defects, or thermodynamic defects. The number of defects increases with the increase in temperature, so are called thermodynamic defects. They are also called intrinsic defects because deviation from regular arrangement of atoms or ions occurs within the crystal and no external substance is added.
- AgBr is a compound in which both Schottky and Frenkel defects are found because AgBr is highly ionic but there is a great difference in the size of Ag^+ and Br^- .

Calculation of number of Schottky/Frenkel defects

- The number (n) of Schottky defects present in an ionic crystal containing N ions at temperature T is given by:

$$n = Ne^{-E/2KT},$$

where E is the energy required to create these n Schottky defects and K is the Boltzmann constant $= R/N_A$
 $= 1.38 \times 10^{-23} \text{ J K}^{-1}$

- The number (n) of Frenkel defects in an ionic crystal containing N ions and N_i is the number of interstitial sites at a temperature T is given by:

$$n = (N/N_i)^{\frac{1}{2}} e^{-E/2KT}$$

(where E is the energy required to create n Frenkel defects. Knowing the value of E , the fraction n/N can be calculated, e.g., for NaCl at 1000 K, the energies of formation of these defects (i.e., Schottky and Frenkel, respectively) are 2 eV and 3 eV, respectively ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$). AgBr has both Schottky and Frenkel defects. Both defects increase exponentially with increase in temperature.

In NaCl, there are 10^{22} ions and 10^6 Schottky pairs/cm³ at room temperature, i.e., there is one Schottky pair defect per 10^{16} ions.

- The fraction of the surface of a crystal vacancies is given by

$$\frac{n}{N} = e^{-E/RT}$$

Table 1.13 Difference between Schottky and Frenkel defects

Schottky defect		Frenkel defect	
1.	It is due to equal number of cations and anions missing from the lattice sites.	1.	It is due to the missing of ions (usually cations) from the lattice sites and these occupy the interstitial sites.
2.	This results in the decrease in the density of crystal.	2.	It has no effect on the density of crystal.
3.	This type of defect is found in highly ionic compounds with high coordination number and having cations and anions of similar sizes, e.g., NaCl, CsCl, etc.	3.	This type of defect is found in crystal where the difference in the size of cations and anions is very large, e.g., AgCl, AgBr, ZnS, etc.

Non-Stoichiometric Defects

If an imperfection causes the ratio of cations and anions to become different from that indicated by the ideal chemical formula, the defect is called non-stoichiometric. Non-stoichiometric defects occurs as follows:

- Metal excess defects
- Metal deficiency defects

Metal excess defects

Metal excess defect may occur in either of the following two ways:

- By anion vacancies or F-centre

A negative ion may be missing from its lattice site, leaving a hole, which is occupied by an electron thereby maintaining an electrical balance. The trapped electrons are called F-centres (from the German word Farbenzentrum for colour centres) because they are responsible for imparting colour to the crystal Fig. 1.73. This defect is similar to Schottky defect and is found in crystals having Schottky defects.

Example: NaCl when heated in Na vapour atmosphere, the excess Na atom deposit on the surface. Now $\text{Cl}^\ominus$ diffuse to the surface where they combine with Na atoms which lose the electrons. The electrons diffuse into the vacant sites created. The electrons absorb some energy from the visible light and re-emit the complimentary yellow colour to NaCl crystal. Excess of Li in LiCl gives a pink colour. Excess of K in KCl make it violet.

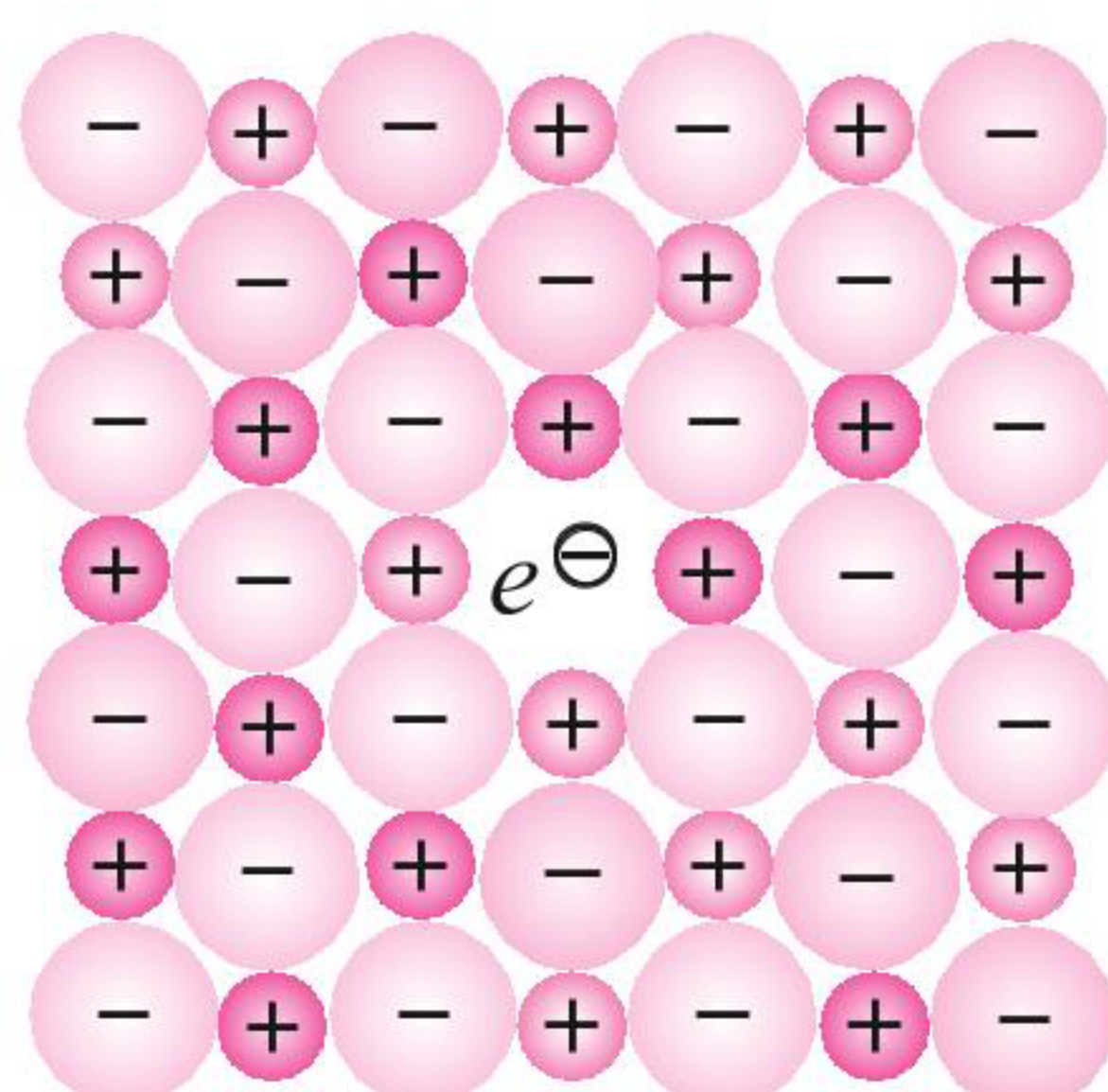


Fig. 1.73 An F-centre in a crystal

b. By the presence of extra cations in interstitial sites

Extra cations occupying interstitial sites with electrons present in another interstitial site to maintain electrical neutrality causes metal excess defects (Fig. 1.74). This defect is similar to Frenkel defect and is formed in crystals having Frenkel defects.

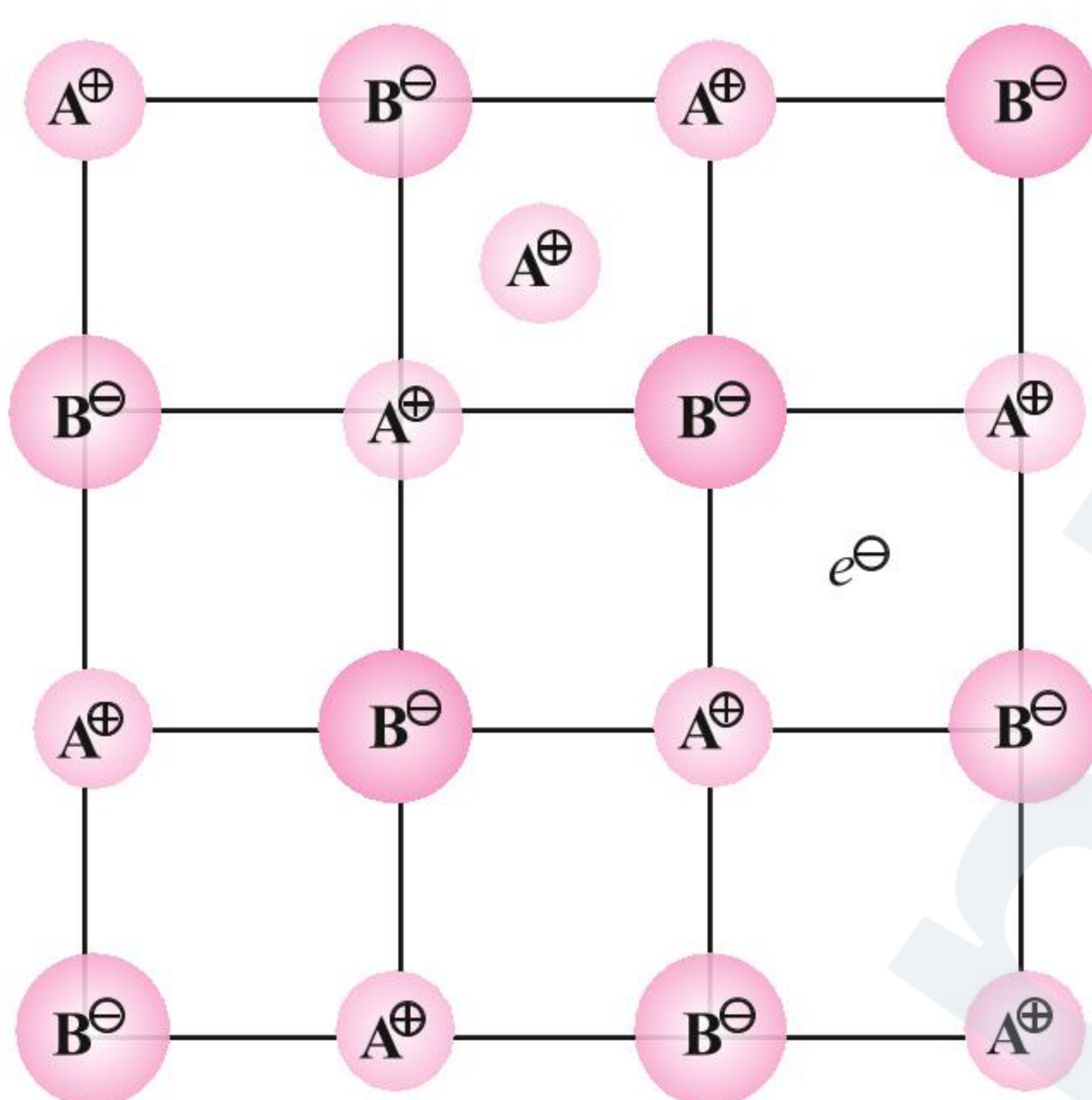
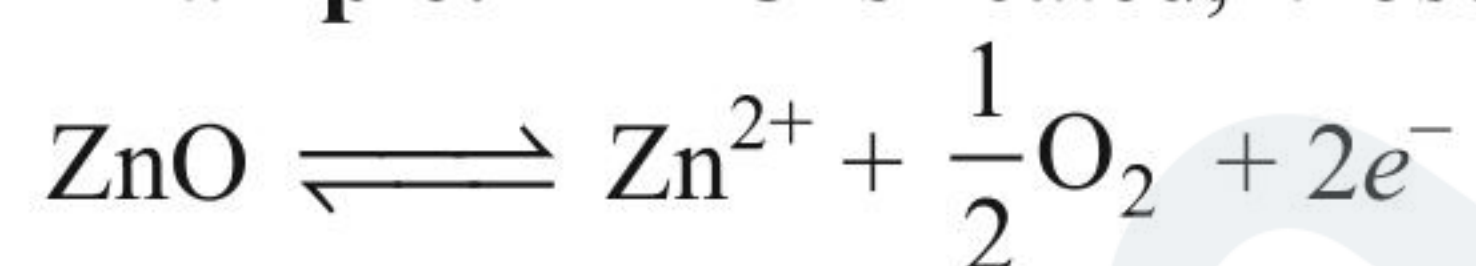


Fig. 1.74 Metal excess defect caused by extra cation in interstitial position

Example: If ZnO is heated, it loses oxygen and turns yellow.



Now there is excess of Zn^{2+} in the crystal and its formula becomes $\text{Zn}_{(1+x)}\text{O}$.

The excess Zn^{2+} ions thus formed get trapped into the vacant interstitial sites while electrons are entrapped in the neighbouring interstitial sites these entrapped electrons increase the electrical conductivity of ZnO and turn yellow. On cooling, they again turn into white due to the reverse reaction as shown above.

Note: Crystals with either type of metal excess defect act as semiconductors.

Metal deficiency defects

This defect occurs when metals show variable valency. It occurs due to the missing of a cation from its lattice site and presence of a cation with higher charge (e.g., +2 instead of +1) in the adjacent site (Fig. 1.75).

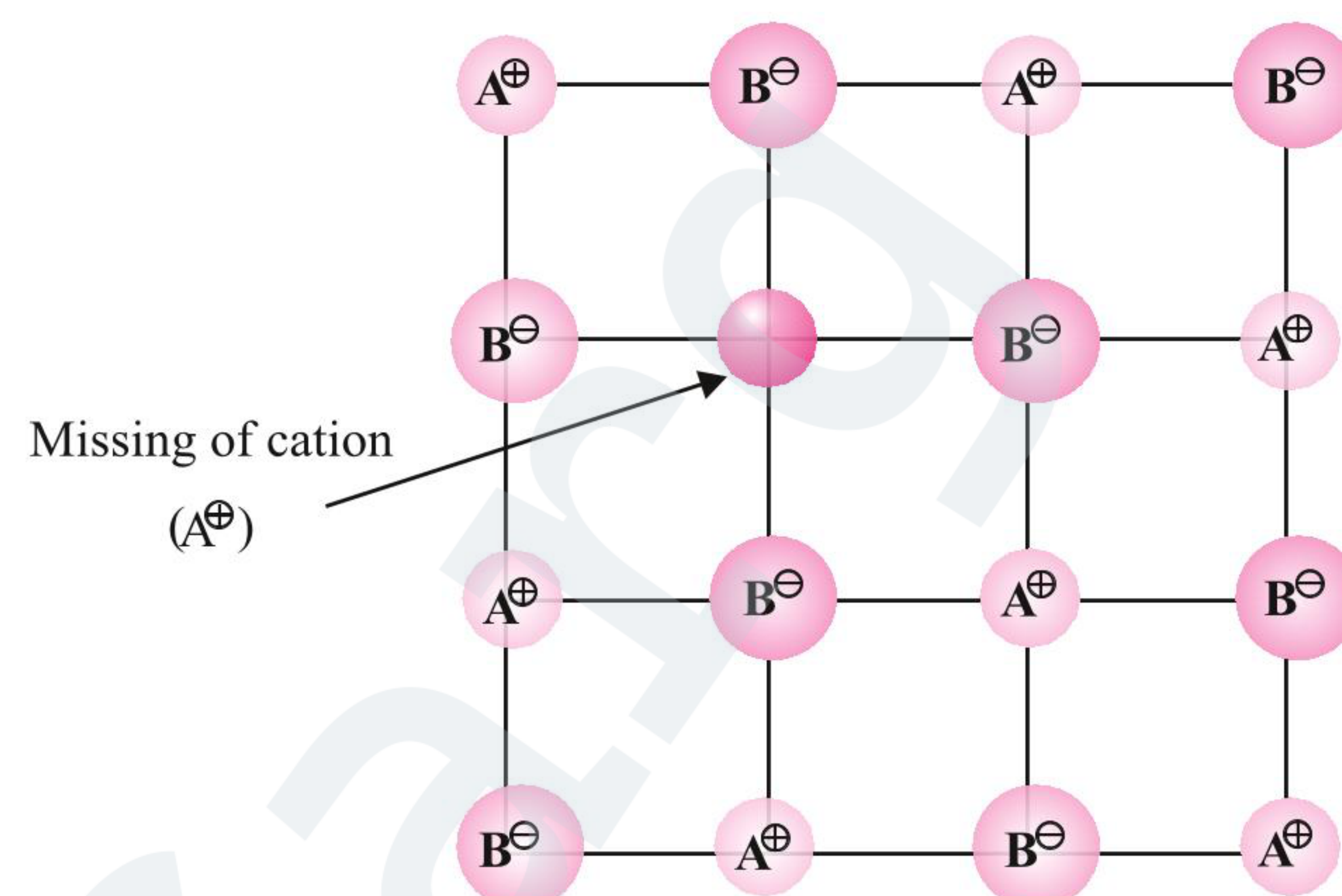


Fig. 1.75 Metal deficiency defect due to the missing of a cation of lower valency and presence of a cation of higher valency

There are many solids which are difficult to prepare in the stoichiometric composition and contain less amount of the metal as compared to the stoichiometric proportion. For example, FeO is found with a composition of $\text{Fe}_{0.95}\text{O}$. It ranges from $\text{Fe}_{0.93}\text{O}$ to $\text{Fe}_{0.96}\text{O}$. In the crystals of FeO, some Fe^{2+} cations are missing and the loss of positive charge is made up with the presence of the required number of Fe^{3+} ions.

Example: Transition elements, FeO, FeS, and NiO.

Impurity Defects

These defects arise when foreign atoms are present at the lattice sites (in place of host atoms) or at the vacant interstitial sites. The formation of former depends upon the electronic structure of the impurity while that of the latter on the size of the impurity.

Introducing impurity defect in covalent solids

Group 13 elements such as Ga and Al and Group 15 elements such as P and As can enter the crystal structure of Group 14 elements Ge or Si substitutionally.

Group 15 elements have one excess valence electrons as compared to Group 14 elements (Si or Ge). Therefore, after forming four covalent bonds, one electron remains in excess which gives rise to electrical conduction.

Group 13 elements have one valence electron less compared to Group 14 elements leading to electron-deficient bond or a hole. Such holes can move across the crystal giving rise to electrical conductivity.

Group 14 elements doped with Group 15 elements are called *n*-type semiconductors, where the symbol *n* indicating negative charge which flows in them. Group 14 elements doped with group 13 elements are called *p*-type semiconductors, the symbol *p* indicating positive hole movement.

Introducing impurity defect in ionic solids

In case of ionic solids, the impurities are introduced by adding impurity of ions. If the impurity ions are in a different oxidation state from that of the host ions, vacancies are created (Fig. 1.76).

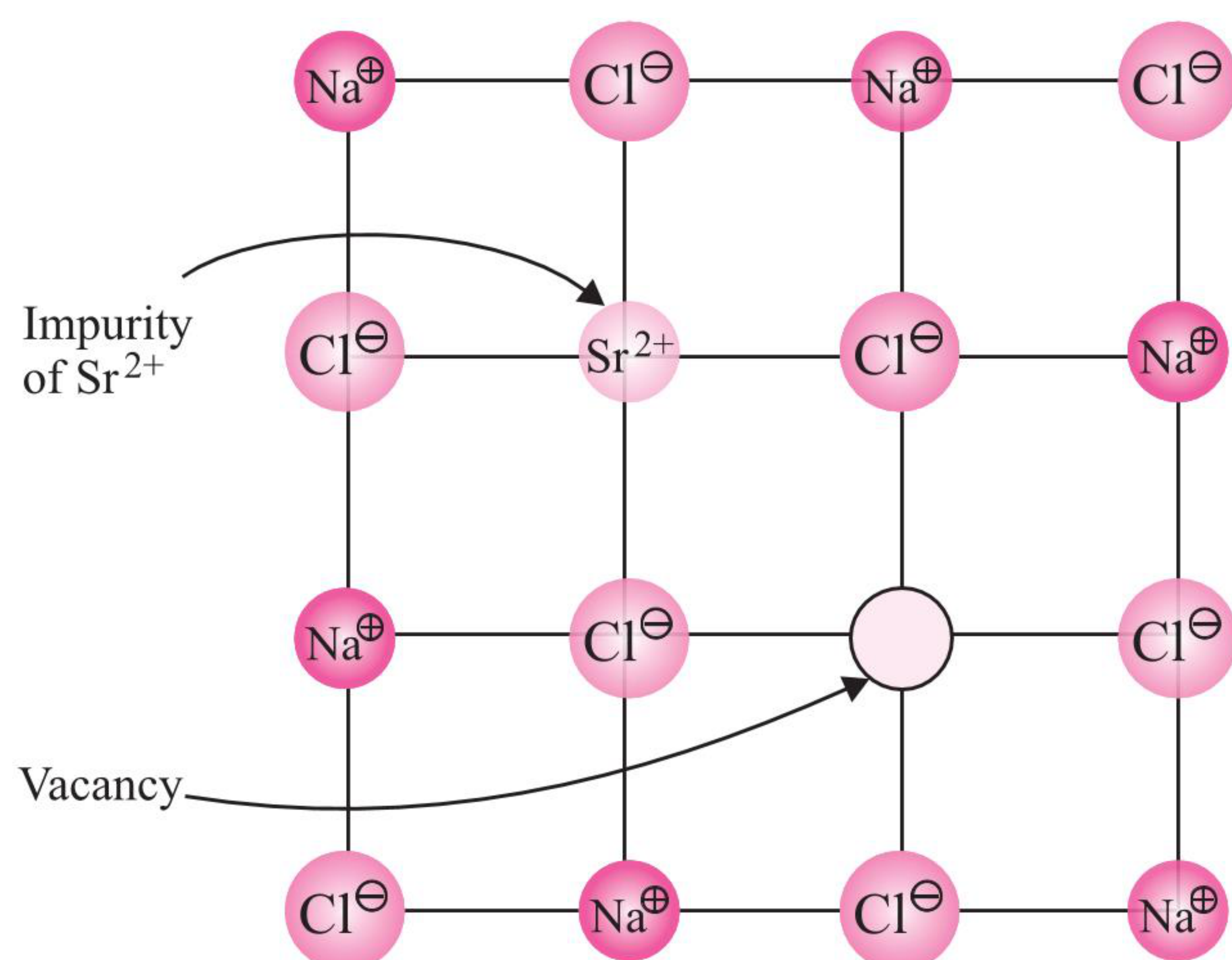


Fig. 1.76 Impurity defect

Example: If molten NaCl, containing a little of SrCl_2 as impurity, is allowed to cool, in the crystals of NaCl formed, at some lattice sites Na^+ ions are substituted by Sr^{2+} ions. For every Sr^{2+} , thus introduced, two Na^+ ions are removed to maintain electrical neutrality, one of these lattice sites is occupied by Sr^{2+} ion and the other remains vacant. These vacancies result in the higher electrical conductivity of the solid.

1.26.3 LINE DEFECTS OR DISLOCATIONS

In addition to the point defects, many solids especially metals possess line defects or also called dislocations. The two important types of linear defects are *edge dislocation* and *screw dislocation*. Both result from the improper orientation of planes with respect to one another in the crystal.

An edge dislocation [Fig. 1.77(a)] is named so because due to this defect this edge of an atomic plane terminates within the crystal instead of passing all the way through.

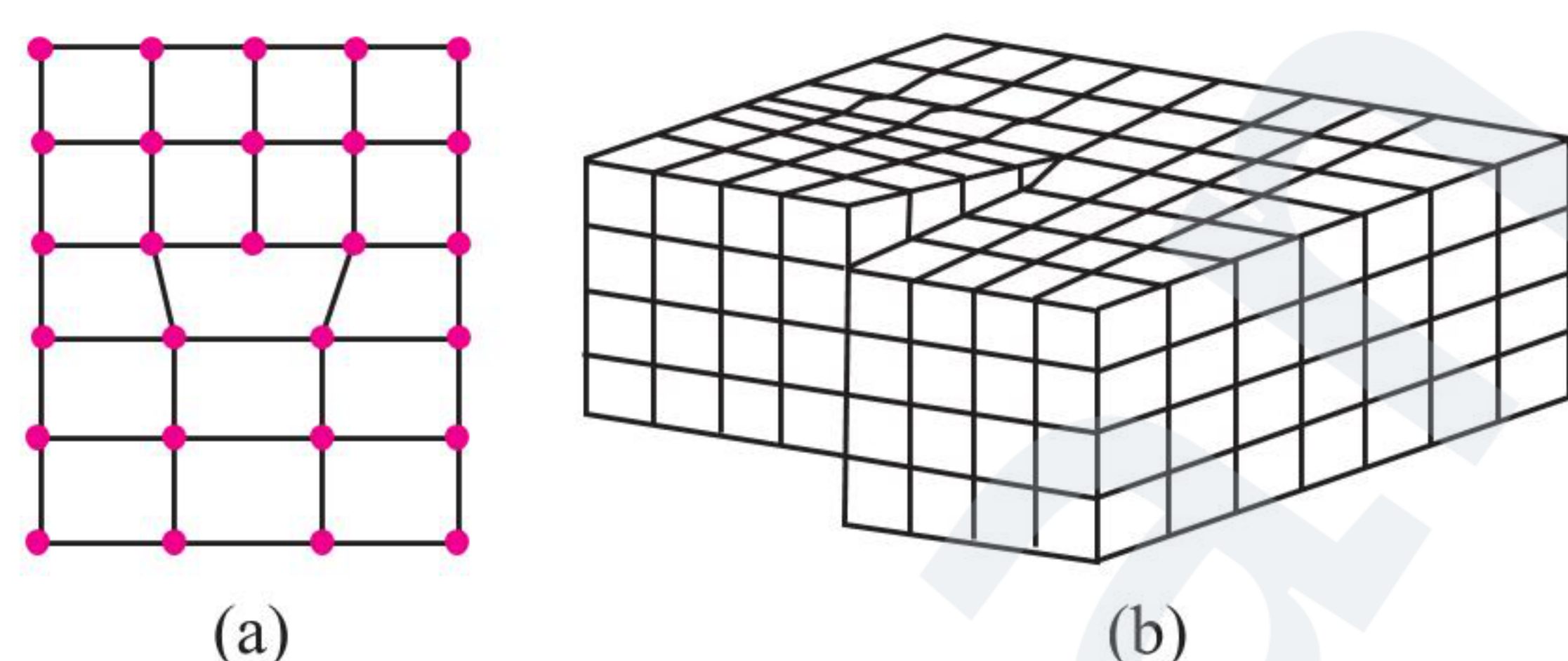


Fig. 1.77 (a) Edge dislocation and (b) screw dislocation

The screw dislocation [Fig. 1.77(b)] is so called because due to this defect, parallel atomic planes perpendicular to the axis are converted into a kind of helical ramp (during the formation of the crystal).

The linear defect or dislocation reduces the strength of the metal considerably. Even the chemical reactions that occur at the surface of the crystal tend to occur at the site of dislocations.

ILLUSTRATION 1.59

If NaCl is doped with 10^{-2} mol% SrCl_2 , what is the concentration of the cation vacancies?

Sol. Doping of NaCl with 10^{-2} mol % SrCl_2 means that 100 mol of NaCl are doped with 10^{-2} mol of SrCl_2 .

$$\therefore 1 \text{ mol of NaCl is doped with } \text{SrCl}_2 = \frac{10^{-2}}{100} = 10^{-4} \text{ mol}$$

As each Sr^{2+} ion introduces one cation vacancy, therefore, the concentration of cation vacancies

$$\begin{aligned} &= 10^{-4} \text{ mol/mol of NaCl} \\ &= 10^{-4} \times 6.023 \times 10^{23} \text{ mol}^{-1} \\ &= 6.02 \times 10^{19} \text{ mol}^{-1} \end{aligned}$$

ILLUSTRATION 1.60

If NaCl is doped with 10^{-3} mol% GaCl_3 , what is the concentration of the cation vacancies?

Sol. 100 mol of NaCl are doped with 10^{-3} mol of GaCl_3 .

$$\therefore 1 \text{ mol of NaCl is doped with } \text{GaCl}_3 = \frac{10^{-3}}{100} = 10^{-5} \text{ mol}$$

As one Ga^{3+} ion is introduced, three Na^+ have to be removed to maintain the electrical neutrality. So as one vacancy is filled by Ga^{3+} , two cation vacancies are formed.

$\therefore$ Concentration of cation vacancy

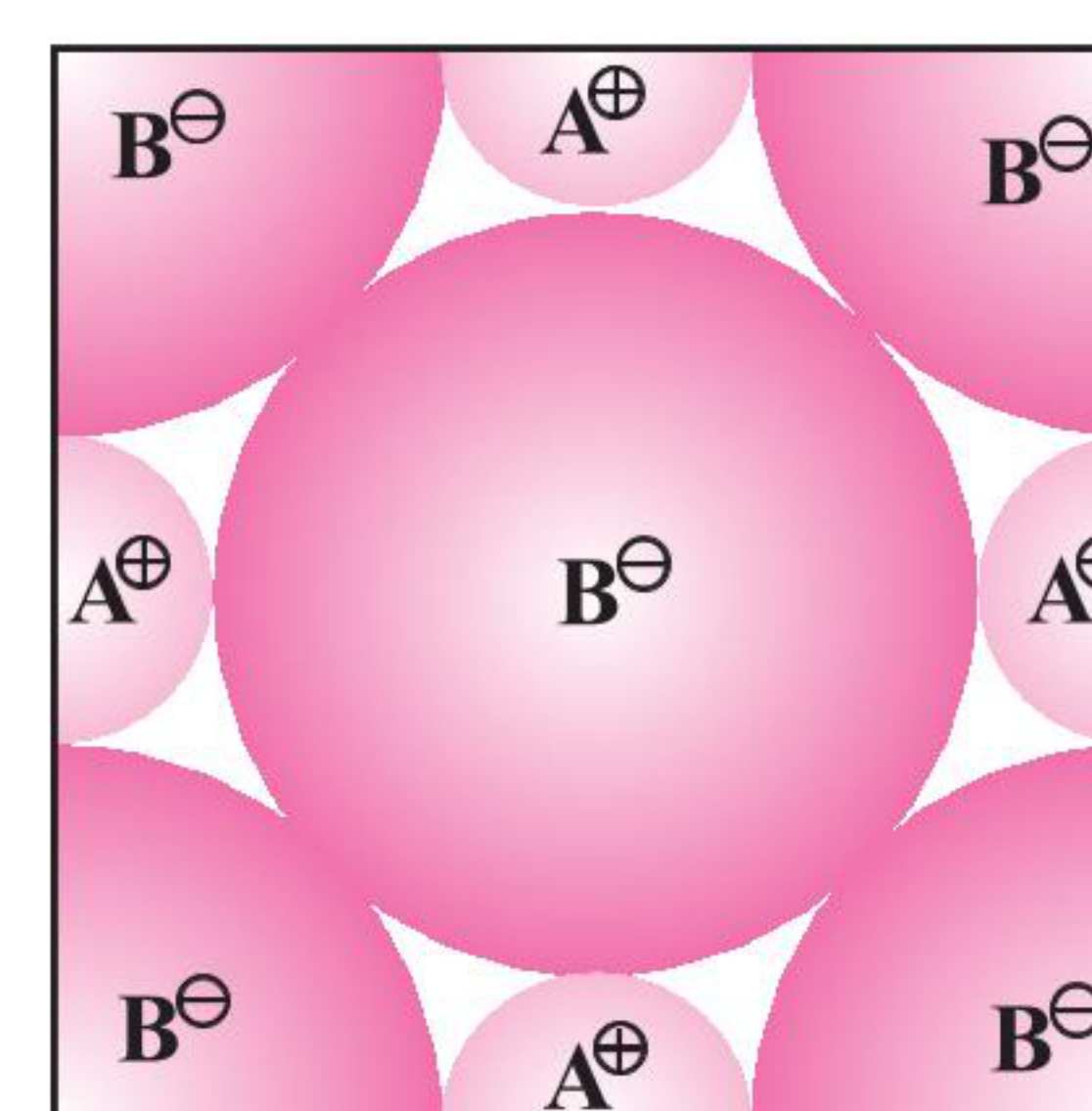
$$\begin{aligned} &= 2 \times 10^{-5} \text{ mol/mol of NaCl} \\ &= 2 \times 10^{-5} \times 6.023 \times 10^{23} \text{ mol}^{-1} \\ &= 12.046 \times 10^{18} \text{ mol}^{-1} \\ &= 1.2046 \times 10^{19} \text{ mol}^{-1} \end{aligned}$$

ILLUSTRATION 1.61

If all the atoms touching one face plane are removed in solid A^+B^- having rock salt type structure, then the formula of the compound left and the defect brought by this removal, respectively, is

- | | |
|------------------------|---|
| a. AB, Frenkel defect | b. A_2B , Frenkel defect |
| c. AB, Schottky defect | d. A_2B , Schottky defect |

Sol. c. i. Since A^+B^- has NaCl-type (fcc) structure. So B^- are in fcc arrangement.



Removed atoms from one of the face

$$\text{Number of } \text{B}^- \text{ ions} = 4$$

$$(\text{Corner} + \text{face centre} = 1 + 3 = 4)$$

$$\text{Number of } \text{A}^+ \text{ ions} = 4$$

$$\begin{aligned} &[\text{in OV formed at body centre} \\ &+ \text{edge centre} = 1 + 3 = 4] \end{aligned}$$

$$\text{Number of } \text{B}^- \text{ ions removed}$$

$$= 4 \text{ corner} \times \frac{1}{8} \text{ per corner share}$$

$$+ 1 \text{ face centre} \times \frac{1}{2} \text{ per face centre share}$$

$$= \frac{4}{8} + \frac{1}{2} = 1$$

Number of $B^{\ominus}$ left = $4 - 1 = 3$

Number of $A^{\oplus}$ ions removed

$$= 4 \text{ edge centre} \times \frac{1}{4} \text{ per edge centre share} = \frac{4}{4} = 1$$

Number of $A^{\oplus}$ ions left = $4 - 1 = 3$

Thus, formula = $A_3B_3 = 3AB$.

ii. As atoms (or ions) are completely removed.

Hence, the defect in the crystal is Schottky type.

ILLUSTRATION 1.62

The addition of $CaCl_2$ crystal to a KCl crystal

- Lowers the density of the KCl crystal
- Raises the density of the KCl crystal
- Does not affect the density of the KCl crystal
- Increases the Frenkel defects of the KCl crystal

Sol. a. One Ca^{2+} lets two $K^{\oplus}$ leave the crystal to maintain the electrical neutrality of the compound.

The mass of two $K^{\oplus}$ is greater than the mass of Ca^{2+} . Hence, density decreases.

ILLUSTRATION 1.63

What fraction of the surface of a crystal of Cd at $T = 298$ K consists of vacancies? Assume that the energy needed to form a vacancy = 0.5 . For Cd(s), $\Delta_{\text{sub}}H^{\ominus} = 112.0 \text{ kJ mol}^{-1}$.

Sol. The number of vacancies (or Schottky defects) (n) is given by.

$$n = Ne^{-E/2KT} \text{ or } \frac{n}{N} = e^{-E/2KT}$$

But fraction of the surface of a crystal vacancy is given by

$$\frac{n}{N} = e^{-E/RT} = \exp \left[\frac{-(0.5)(112.0 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} \right] = 1.5 \times 10^{-10}$$

ILLUSTRATION 1.64

Calcium crystallizes in fcc unit cell with 0.556 nm . Calculate the density if

- It contains 0.2% Frenkel defects
- It contains 0.1% Schottky defects

Sol.

- Frenkel defects do not change the value of the theoretical density because the atom is occupying an interstitial position instead of a lattice position.

- Z_{eff} of Ca = 4 atoms/unit cell (since it is fcc type)

Since there are 0.1% Schottky defects,

$$\text{So } Z_{\text{eff}} = \left(4 - \frac{0.1}{100} \times 4 \right) = 3.996$$

$$\therefore \rho = \frac{Z_{\text{eff}} \times Aw}{N_A \times a^3} \quad (\because 1 \text{ nm} = 10^{-9} \text{ m} = 10^{-7} \text{ cm})$$

$$= \frac{(3.996) \times 40 \text{ g}}{(6 \times 10^{23} \text{ mol}^{-1})(0.556 \text{ nm} \times 10^{-7} \text{ cm})^3} = 1.547 \text{ g cm}^{-3}$$

1.27 ELECTRICAL PROPERTIES OF SOLIDS

Solids exhibit various range of electrical conductivities, extending over 27 orders of magnitude ranging from 10^{-20} to $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$. Solids are classified into three types on the basis of their conductivities.

- Conductors:** The solids with conductivities ranging between 10^4 and $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ are called conductors. Metals having conductivities in the order of $10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ are good conductors.
- Insulators:** These are the solids with very low conductivities ranging between 10^{-20} and $10^{-10} \text{ ohm}^{-1} \text{ m}^{-1}$.
- Semiconductors:** These are the solids with conductivities in the intermediate range from 10^{-6} to $10^4 \text{ ohm}^{-1} \text{ m}^{-1}$.

1.27.1 CONDUCTION OF ELECTRICITY IN METALS

Metallic conductors conduct electricity through the movement of electrons. Electrolytes conduct electricity through the movement of ions.

Metals conduct electricity in solid as well in as molten state. The conductivity of metals depends upon the number of valence electrons available per atom. The atomic orbitals of metal atoms form molecular orbitals which are so close in energy to each other as to form a *band*. If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, then electrons can flow easily under an applied electric field and the metal shows conductivity [Fig. 1.78(a)].

If the gap between filled valence band and the next higher unoccupied band (conduction band) is large, electrons cannot jump to it and such a substance has very small conductivity. It behaves as an insulator [Fig. 1.78(b)].

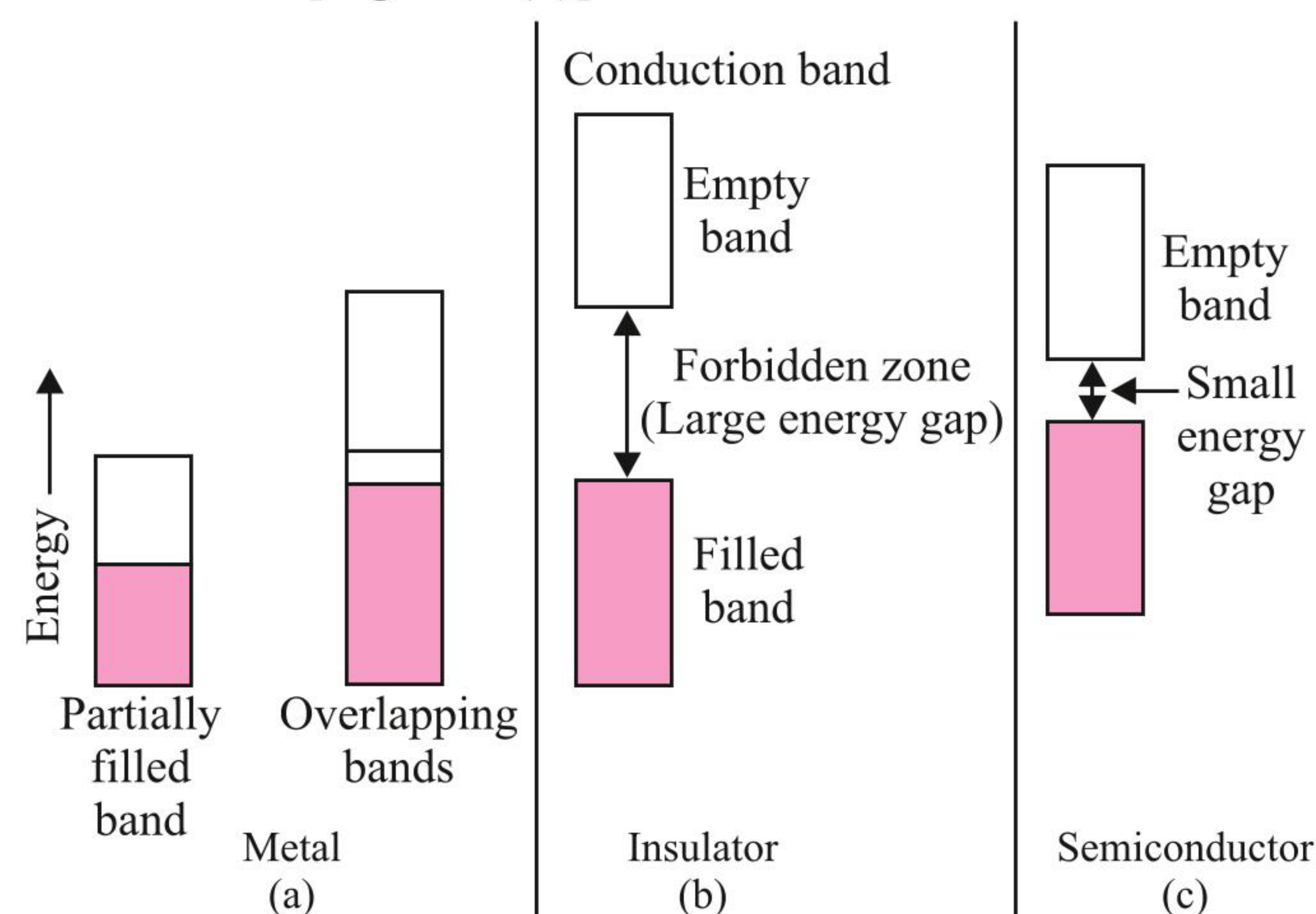


Fig. 1.78 Distinction among (a) metals, (b) insulators, and (c) semi-conductors. In each case, an unshaded area represents a conduction band

1.27.2 CONDUCTION OF ELECTRICITY IN SEMICONDUCTORS

In case of semiconductors, the gap between the valence band and conduction band is small [Fig. 1.78(c)]. Therefore, some electrons may jump to conduction band and show some conductivity. The electrical conductivity of semiconductors increases with rise in temperature, since more electrons can jump to the conduction band, substances such as silicon and germanium show this type of behaviour and are called intrinsic semiconductors.

The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called *doping*. *Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce electronic defects in them.*

1.27.3 ELECTRON-RICH IMPURITIES

Si and Ge belong to Group 14 of the periodic table and have four valence electrons each. In their crystals each atom forms four covalent bonds with its neighbours [Fig. 1.79(a)]. When doped with a group 15 element such as P or As, which contains five valence electrons, they occupy some of the lattice sites in Si or Ge crystal [Fig. 1.79(b)]. Four out of five electrons are used in the formation of four covalent bonds with the four neighbouring Si atoms. The fifth electron is extra and becomes delocalized. These delocalized electrons increase the conductivity of doped Si (or germanium). Here the increase in conductivity is due to the negatively charged electron, hence silicon doped with electron-rich impurity is called *n-type semiconductor* [Fig. 1.80(a)].

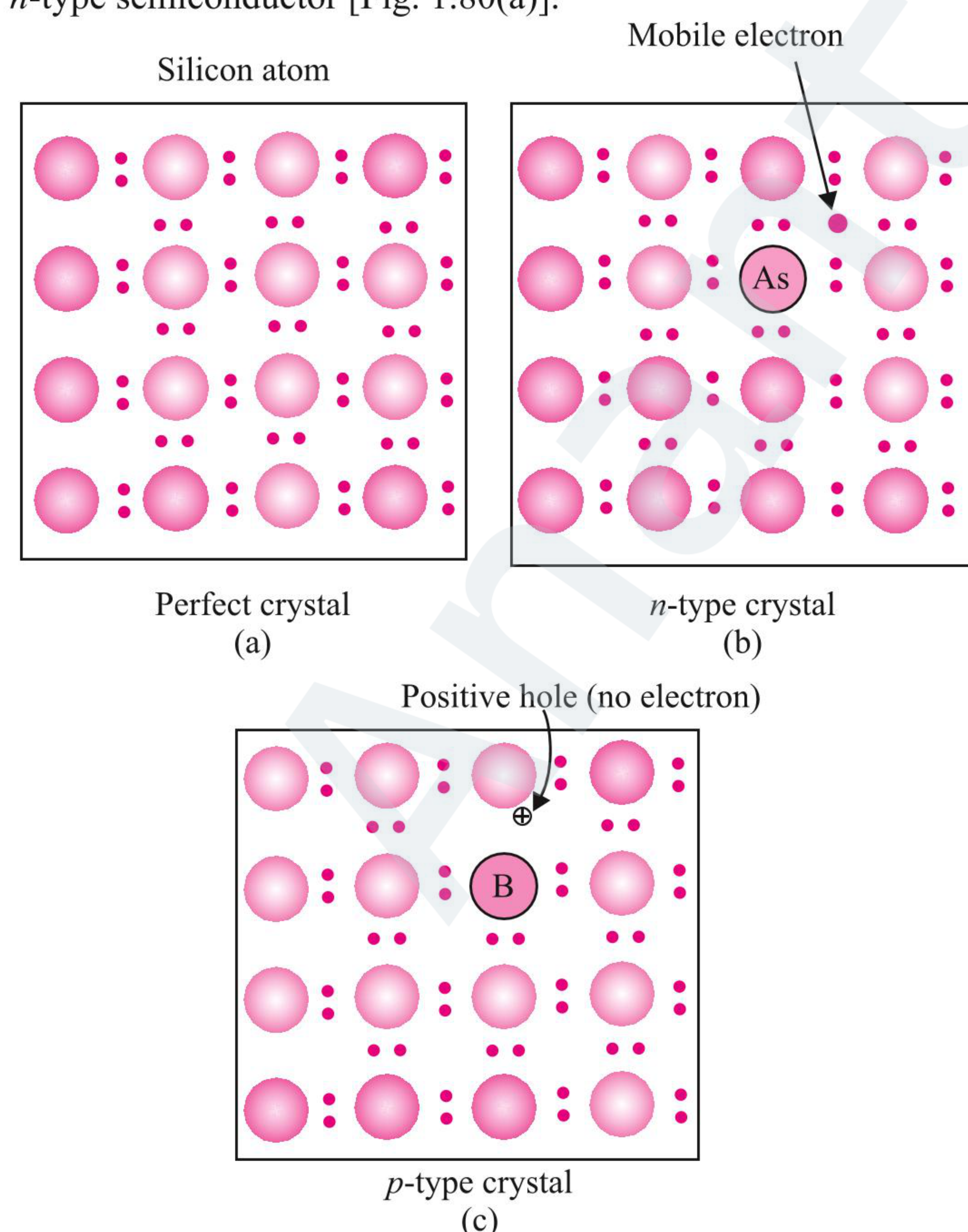


Fig. 1.79 Creation of n-type and p-type semiconductors by doping Group 13 and 15 elements

1.27.4 ELECTRON-DEFICIT IMPURITIES

Si and Ge can also be doped with a group 13 element such as B, Al or Ga which contains only three valence electrons. The place where the fourth valence electron is missing is called electron hole or electron vacancy [Fig. 1.79(c)]. An electron from a neighbouring atom can come and fill the electron hole, but in doing so it would leave an electron hole at its original position.

If it happens it would appear as if the electron hole has moved in the direction opposite to that of the electron that filled it. Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes, but it would appear as if electron holes are positively charged and are moving towards negatively charged plate. This type of semiconductors are called *p-type semiconductors* [Fig. 1.80(b)].

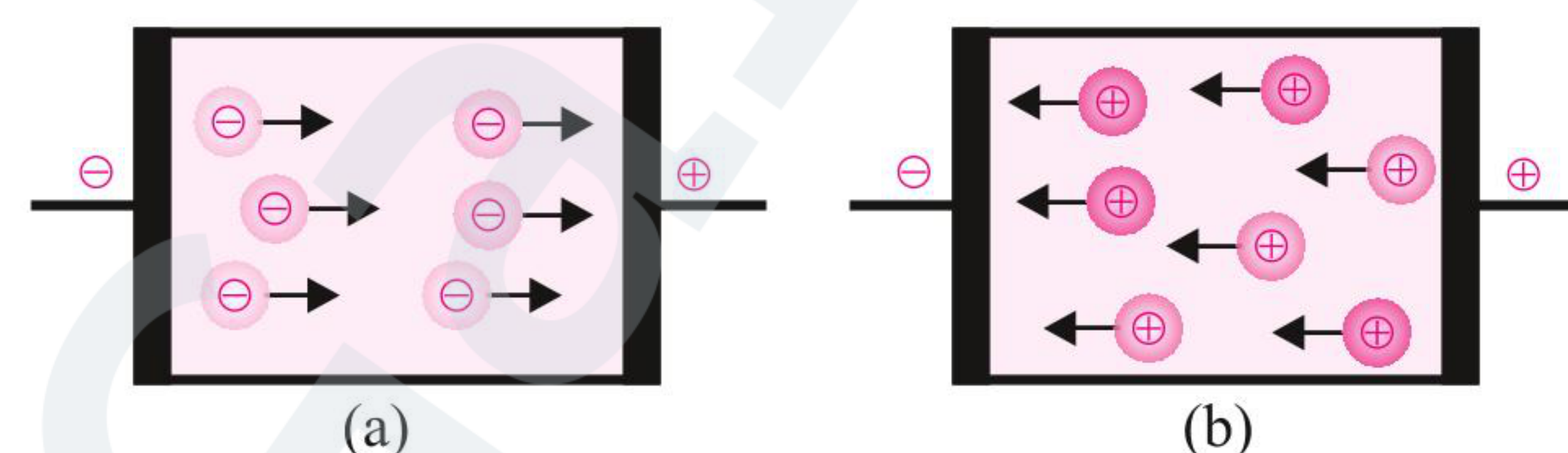


Fig. 1.80 (a) n-type semiconductor and (b) p-type semiconductor

1.27.5 APPLICATIONS OF N-TYPE AND P-TYPE SEMICONDUCTORS

Various combinations of *n*-type and *p*-type semiconductors are used for making electronic components. Diode is a combination of *n*-type and *p*-type semiconductors and is used as a rectifier. Transistors are made by sandwiching a layer of one type of semiconductor between two layers of the other type of semiconductor. *npn* and *pnp* type of transistors are used to detect or amplify radio or audio signals. The solar cell is an efficient photo-diode used for the conversion of light energy into electrical energy.

Ge and Si are Group 14 elements and, therefore, have a characteristic valency of 4 and form four bonds as in diamond. A large variety of solid state materials has been prepared by combination of Groups 13 and 15 or 12 and 16 to simulate average valency of 4 as in Ge or Si. Typical compounds of Groups 13–15 are InSb, AlP, and GaAs. Gallium arsenide (GaAs) semiconductors have very fast response and have revolutionized the design of semiconductor devices. ZnS, CdS, CdSe, and HgTe are examples of Groups 12–16 compounds. In these compounds, the bonds are not perfectly covalent and the ionic character depends on the electronegativities of the two elements.

Transition metal oxides show marked differences in electrical properties. TiO, CrO₂, and ReO₃ behave like metals. Rhenium oxide, ReO₃, is like metallic copper in its conductivity and appearance. Certain other oxides such as VO, VO₂, VO₃, and TiO₃ show metallic or insulating properties depending on temperature.

1.28 MAGNETIC PROPERTIES OF SOLIDS

Every substance has some magnetic properties associated with it. The origin of these properties lies in the electrons. Each electron in an atom behaves like a tiny magnet. Its magnetic moment originates from two types of motion (a) its orbital

motion around the nucleus and (b) its spin around its own axis (Fig. 1.81). Electron being a charged particle and undergoing these motions can be considered as a small loop of current which possesses a magnetic moment. Thus, each electron has a permanent spin and an orbital magnetic moment associated with it. Magnitude of this magnetic moment is very small and is measured in the unit called *Bohr magneton*, μ_B . It is equal to $9.27 \times 10^{-24} \text{ A m}^2$.

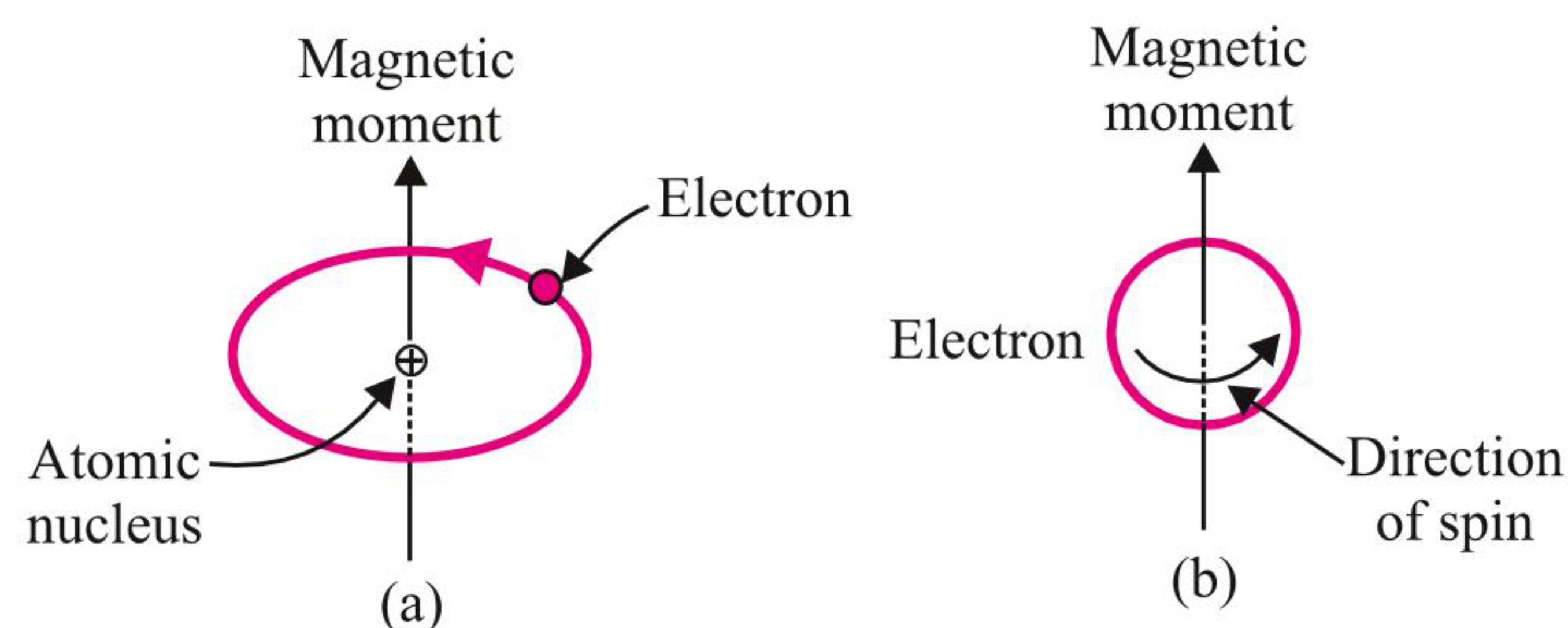


Fig. 1.81 The magnetic moment associated with (a) an orbiting electron and (b) a spinning electron

For each electron in an atom, the spin magnetic moment is $\pm\mu_B$ (depending upon two possibilities of the spin). The contribution of the orbital magnetic moment is equal to $m_l\mu_B$ where m_l is the magnetic quantum number of the electron.

Solids composed of atoms having completely filled electron shells or subshells are not capable of being permanently magnetized. This category includes the noble gases (such as He, Ne, Ar, etc.) as well as some ionic materials.

Solid materials are classified in different categories of magnetic materials based on the response of electron and atomic magnetic dipoles on application of an external applied magnetic field. Magnetic dipoles which may exist in a material can be considered analogous to electric dipoles. Magnetic dipoles may be thought of as small bar magnets composed of north and south poles instead of positive and negative electric charges. In our present discussion, magnetic dipole moment will be represented by arrows as shown in Figs. 1.82(a) and 1.82(b).

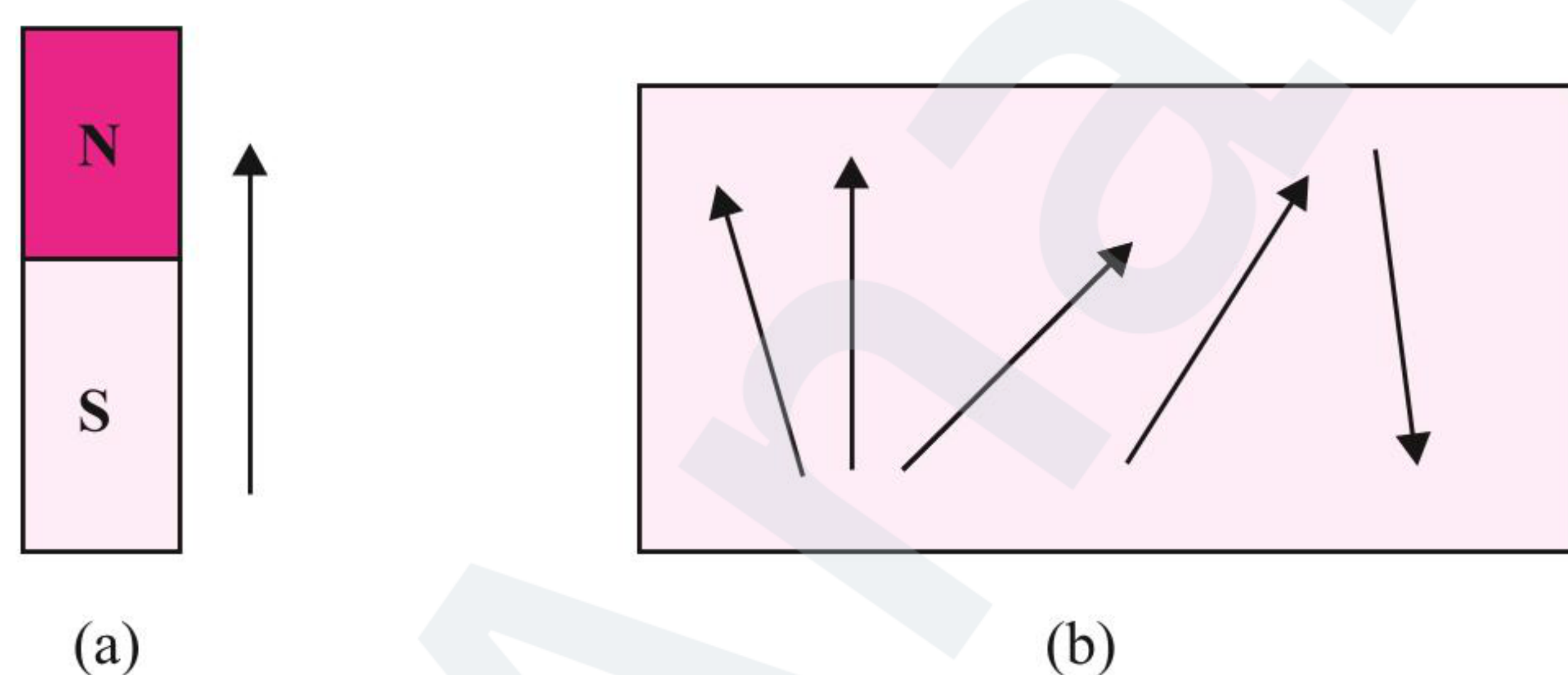


Fig. 1.82 (a) Magnetic moment as designated by an arrow and (b) in a paramagnetic substance

On the basis of their magnetic properties, substances can be classified into five categories: (a) paramagnetic (b) diamagnetic, (c) ferromagnetic, (d) antiferromagnetic, and (e) ferrimagnetic.

1.28.1 PARAMAGNETISM

Paramagnetic substances are weakly attracted by a magnetic field. They are magnetized in a magnetic field in the same direction and lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. For example,

O_2 , Cu^{2+} , Fe^{3+} , Cr^{3+} .

1.28.2 DIAMAGNETISM

Diamagnetic substances are weakly repelled by magnetic field. H_2O , NaCl , and C_6H_6 are some examples of such substances. They are weakly magnetized in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character.

1.28.3 FERROMAGNETISM

A few substances such as Fe, Co, Ni, Gd, and CrO_2 are attracted very strongly by a magnetic field. Such substances are called ferromagnetic substances. Besides strong attractions, these substances can be permanently magnetized. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains. Thus, each domain acts as a tiny magnet. In an unmagnetized piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. When the substance is placed in a magnetic field all the domains get oriented in the direction of the magnetic field [Fig. 1.83(a)] and a strong magnetic effect is produced. This ordering of domains persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

1.28.4 ANTIFERROMAGNETISM

Substances such as MnO showing anti-ferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment [Fig. 1.83(b)].

1.28.5 FERRIMAGNETISM

Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers [Fig. 1.83(c)]. They are weakly attracted by magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites such as MgFe_2O_4 and ZnFe_2O_4 are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.

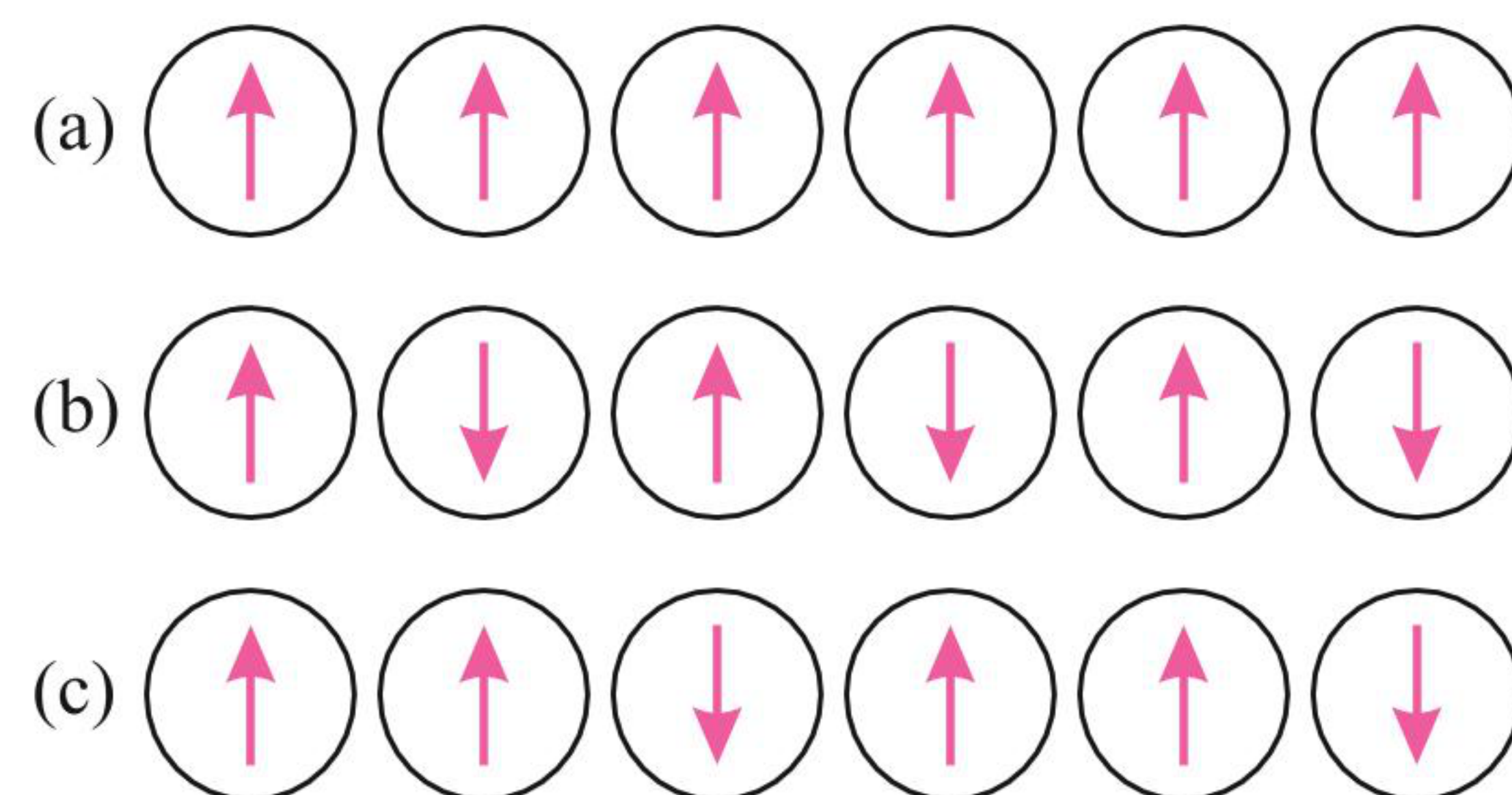


Fig. 1.83 Schematic alignment of magnetic moments in (a) ferromagnetic, (b) antiferromagnetic, and (c) ferrimagnetic substances

Note: All magnetically ordered solids (ferromagnetic, antiferromagnetic, and ferrimagnetic solids) transform to the paramagnetic state at high temperature due to the randomization of spins. Ferrimagnetic material Fe_3O_4 becomes paramagnetic at 850 K. It is also observed that ferromagnetic substances have a characteristic temperature above which no ferromagnetism is observed. This is known as Curie temperature.

1.29 DIELECTRIC PROPERTIES OF SOLIDS

In insulators, electrons are closely bound to individual atoms or ions and they do not generally migrate under an applied electric field. However, dipoles are created by a shift in charges, resulting in polarization. Besides that there may also be permanent dipoles in the crystal. Following situations may arise:

- These dipoles may align themselves in an ordered manner such that there is a net dipole moment in the crystal.
- These dipoles may align themselves in a manner such that dipole moments may cancel each other.
- There are no dipoles in the crystals, but only ions are present.

The crystals where situation (a) is found, exhibit *piezoelectricity* or *pressure electricity*. When such a crystal is deformed by mechanical stress electricity is produced due to the displacement of ion or if an electric field is applied to the crystal, there will be atomic displacement causing mechanical strain. The piezoelectric effect is demonstrated in Fig. 1.84.

Piezoelectric crystals are utilized in transducers devices, that convert electrical energy into mechanical strains or vice versa. Familiar applications that employ piezoelectrics include phonograph pickups, microphones, ultrasonic generators, strain gauges, and sonar detectors.

Piezoelectric materials include titanates of barium and lead, lead zirconate (PbZrO_3), ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), and quartz. Some of the piezoelectric crystals when heated produce small electric potential or *pyroelectricity*.

In some of the piezoelectric crystals, the dipoles are permanently lined up (spontaneously polarized) even in the absence of an electric field, and the direction of polarization can be changed by applying an electric field. The phenomenon is called *ferroelectricity* by analogy with ferromagnetism.

Barium titanate (BaTiO_3), sodium potassium tartrate (Rochelle salt), and potassium dihydrogen phosphate (KH_2PO_4) are ferroelectric solids. If the dipoles align along alternate directions, there will be no net dipole moment and the crystal is said to be *antiferroelectric*. Lead zirconate (PbZrO_3) is a typical antiferroelectric solid.

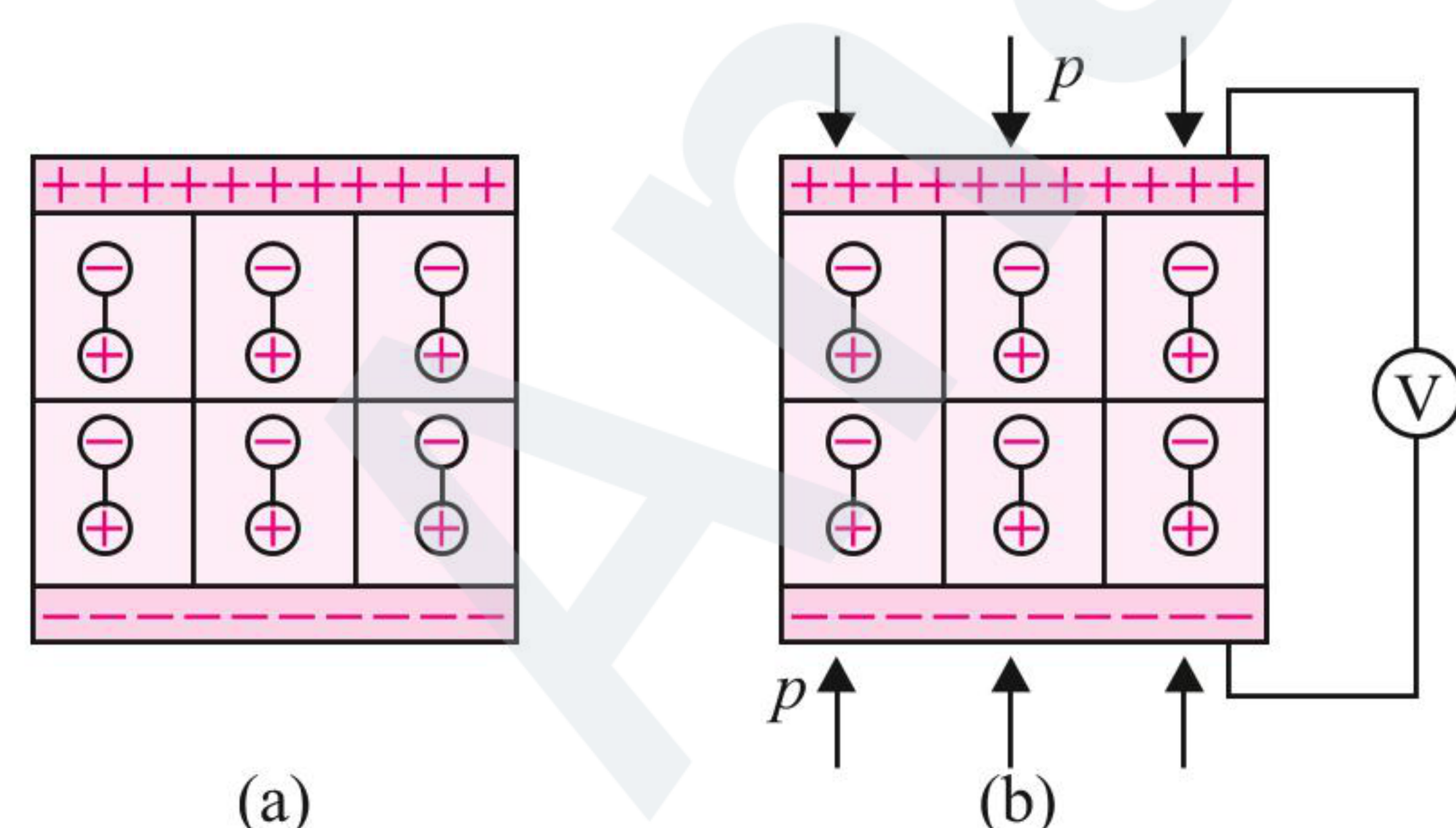


Fig. 1.84 (a) Dipole within a piezoelectric material. (b) A voltage is generated when the material is subjected to a compressive stress (p)

1.29.1 SUMMARIZATION OF DIELECTRIC PROPERTIES OF POLAR CRYSTALS

Insulators do not conduct electricity because the electrons present in them are held tightly to the individual atoms or ions and are not

free to move. However when electric field is applied, polarization takes place because the nucleus is attracted toward cathode and electron cloud toward anode as shown in Fig. 1.85.

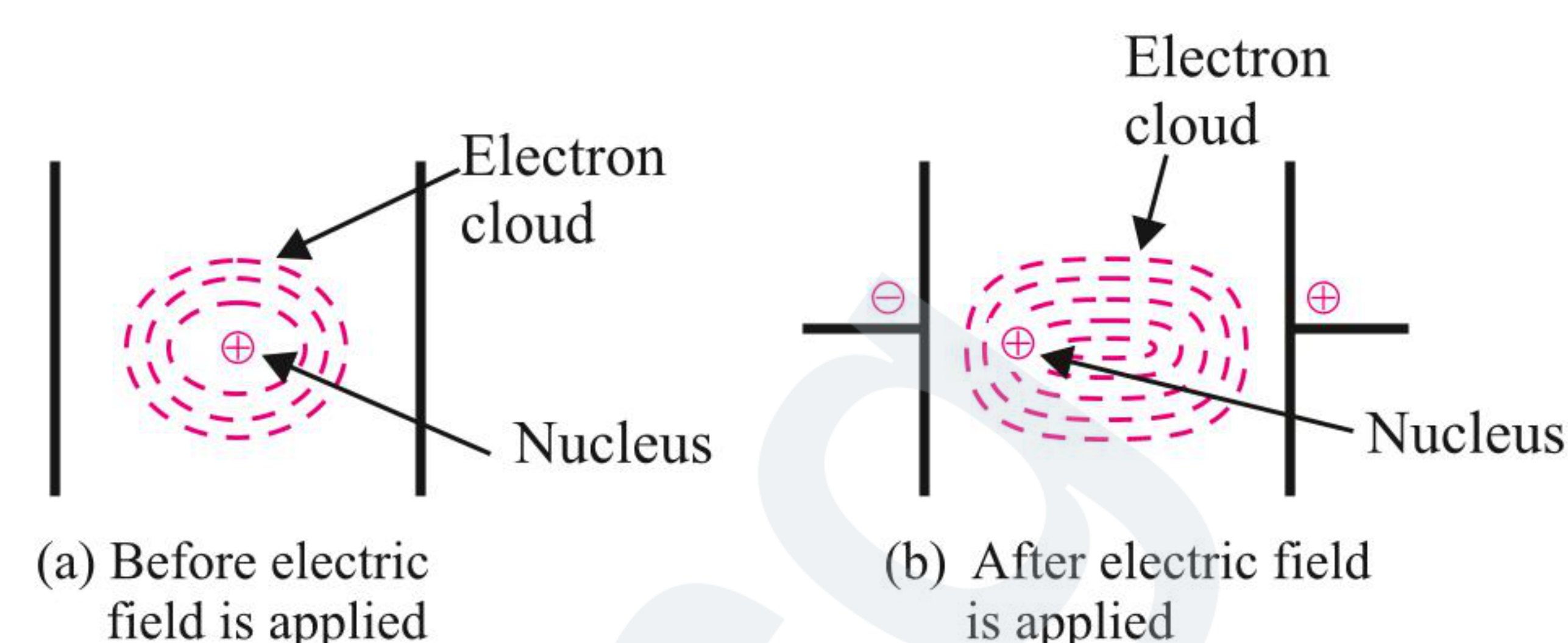


Fig. 1.85 These formed dipoles may align themselves in an ordered manner so that the crystal has a net dipole moment

Such polar crystals show following electrical properties:

- Piezoelectricity:** When these crystals are subjected to mechanical stress, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity and the crystals are called piezoelectric crystals. But if an electric field is applied to these crystals, there will be atomic displacement causing mechanical strain.
 - Pyroelectricity:** Some polar crystals when heated produce a small current or pyroelectricity.
 - Ferroelectricity:** In some piezoelectric crystals, the dipoles are permanently lined up even in the absence of an electric field. However, on applying electric field the direction of polarization changes, e.g., BaTiO_3 , sodium potassium tartrate (Rochelle salt).
- Note:** All ferroelectric solids are piezoelectric, but the reverse is not true.
- Antiferroelectricity:** If there is no net dipole moment it is said to be an antiferroelectric crystal. This is because the dipoles are alternately arranged. For example, lead zirconate (PbZrO_3).
 - Superconductivity:** When the electrical resistance of materials becomes almost zero, the material becomes superconductor. The temperature at which the material shows superconductivity is called *transition temperature*, e.g., $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 90 K.

Table 1.14 Examples of some common magnetic and dielectric substance.

Type of substance	Examples
1. Diamagnetic	N_2 , NaCl , Zn , Cd , Cu^+ , TiO_2
2. Paramagnetic	Transition metals (Cr , Mn , Ni , Co , Fe) metal ions (Cu^{2+} , Ni^{2+} , Fe^{3+}), metal oxides (CuO , VO_2), molecules (NO and O_2)
3. Ferromagnetic	Ni , Fe , Co , CrO_2
4. Antiferromagnetic	MnO , Mn_2O_3 , MnO_2
5. Ferrimagnetic	Fe_3O_4 and pyrites
6. Ferroelectric and piezoelectric	Rochelle salt (sodium potassium tartrate), KH_2PO_4 , BaTiO_3
7. Antiferroelectric	PbZrO_3 (lead zirconate)

CONCEPT APPLICATION EXERCISE 1.2

1. The number of Schottky defects (n) present in an ionic compound containing N ions at temperature T is given by $n = Ne^{-E/2KT}$, where E is the energy required to create n Schottky defects and K is the Boltzmann constant. If the mole fraction of Schottky defect in NaCl crystal at 2900 K is X , then calculate $-\ln(x)$.

Given: ΔH of Schottky defect = 2 eV and

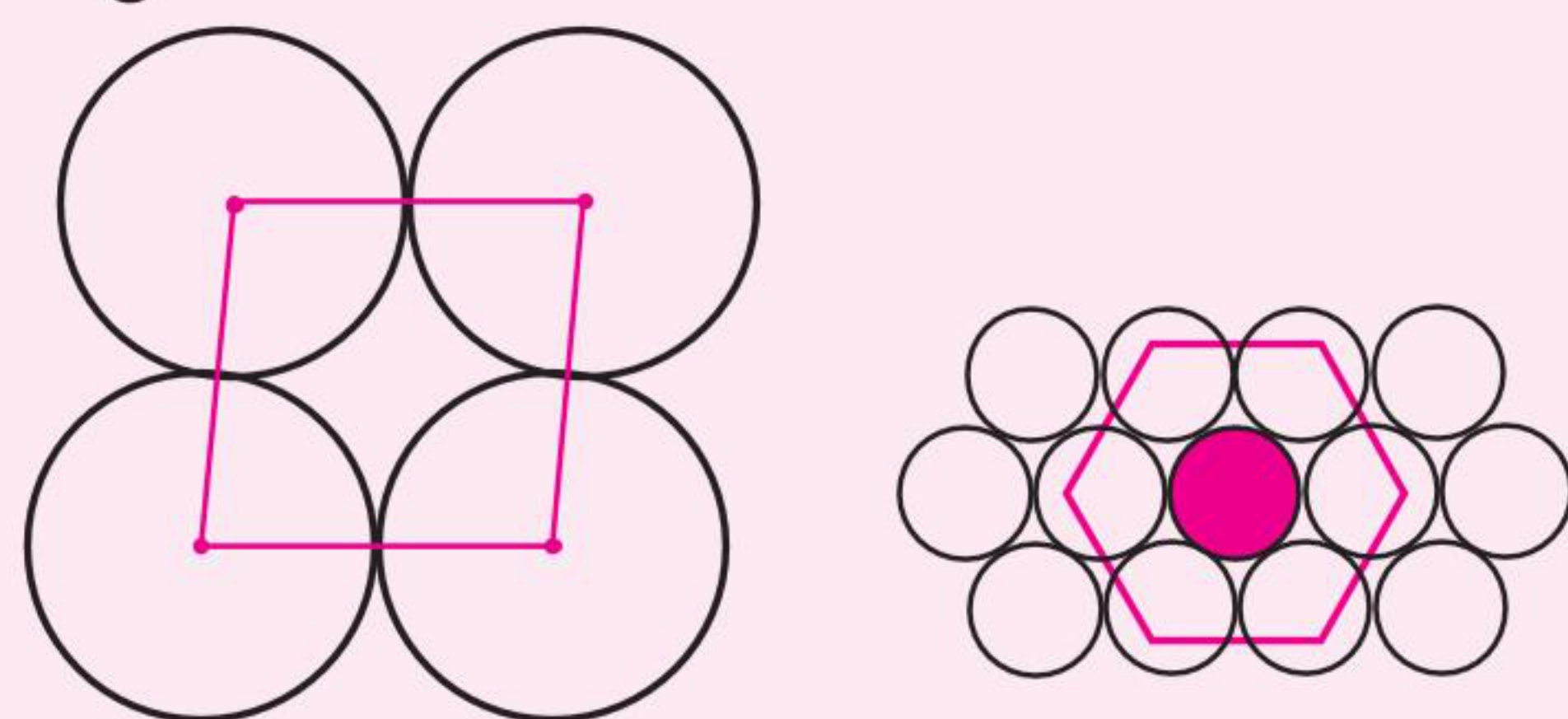
$$K = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

$$1 \text{ eV} = 1.608 \times 10^{-19} \text{ J}$$

2. FeO crystallizes in NaCl-type of crystal lattice. The crystals of FeO are deficient in iron and are always non-stoichiometric. Some cationic sites are vacant and some contain Fe^{3+} ions but the combination is such that the structure is electrically neutral. The formula approximates to $\text{Fe}_{0.95}\text{O}$.

- What is the ratio of Fe^{2+} to Fe^{3+} ions in the solid?
- What percentage of cation sites are vacant?

3. i. What is the relation between the radius of circle and the length of parallelogram for the unit cell shown in figure below?



- How many nearest neighbour circle does a given circle have in the second figure above?
4. i. Why is coordination number of 12 not found in ionic crystals?
- Out of NaCl and CsCl, which one is more stable and why?
5. How would you account for the following?
- Frenkel defects are not found in alkali metal halides.
 - Schottky defects lower the density of related solids.
6. a. What is levitation?
- b. In what condition, mercury starts behaving as a superconductor?

7. The length of a unit cell in the nickel crystal is 0.352 nm. Diffraction of X-rays of 0.154 nm wavelength from a nickel crystal occurs at 22.2° , 25.9° and 38.2° . Show that these data are consistent with a face-centered cubic crystal structure.

8. Which oxide is used to make magnetic tapes? Which kind of magnetism is shown by this oxide?

9. If edge fraction unoccupied in ideal anti-fluorite structure is X . Calculate the value of Z . Where $Z = \frac{X}{0.097}$

10. Ionic solid Na^+A^- crystallise in rock salt type structure. 2.592 gm of ionic solid salt NaA dissolved in water to make 2 litre solution. The pH of this solution is 8. If distance between cation and anion is 300 pm, calculate density of ionic solid (in gm/cm^3).

(Given: $pK_w = 13$, $pK_a(\text{HA}) = 5$, $N_A = 6 \times 10^{23}$)

11. Calculate the value of $\frac{Z}{20}$. Where

Z = Co-ordination number of 2D-square close packing

+

Co-ordination number of 2D-hcp

+

Co-ordination number of 3D-square close packing

+

Co-ordination number of 3D, ABCABC..... packing

+

Co-ordination number of 3D, ABAB..... packing

12. You are given marbles of diameter 10 mm. They are to be placed such that their centres are lying in a square bound by four lines each of length 40 mm. What will be the arrangements of marbles in a plane so that maximum number of marbles can be placed inside the area? Sketch the diagram and derive expression for the number of molecules per unit area.

ANSWERS

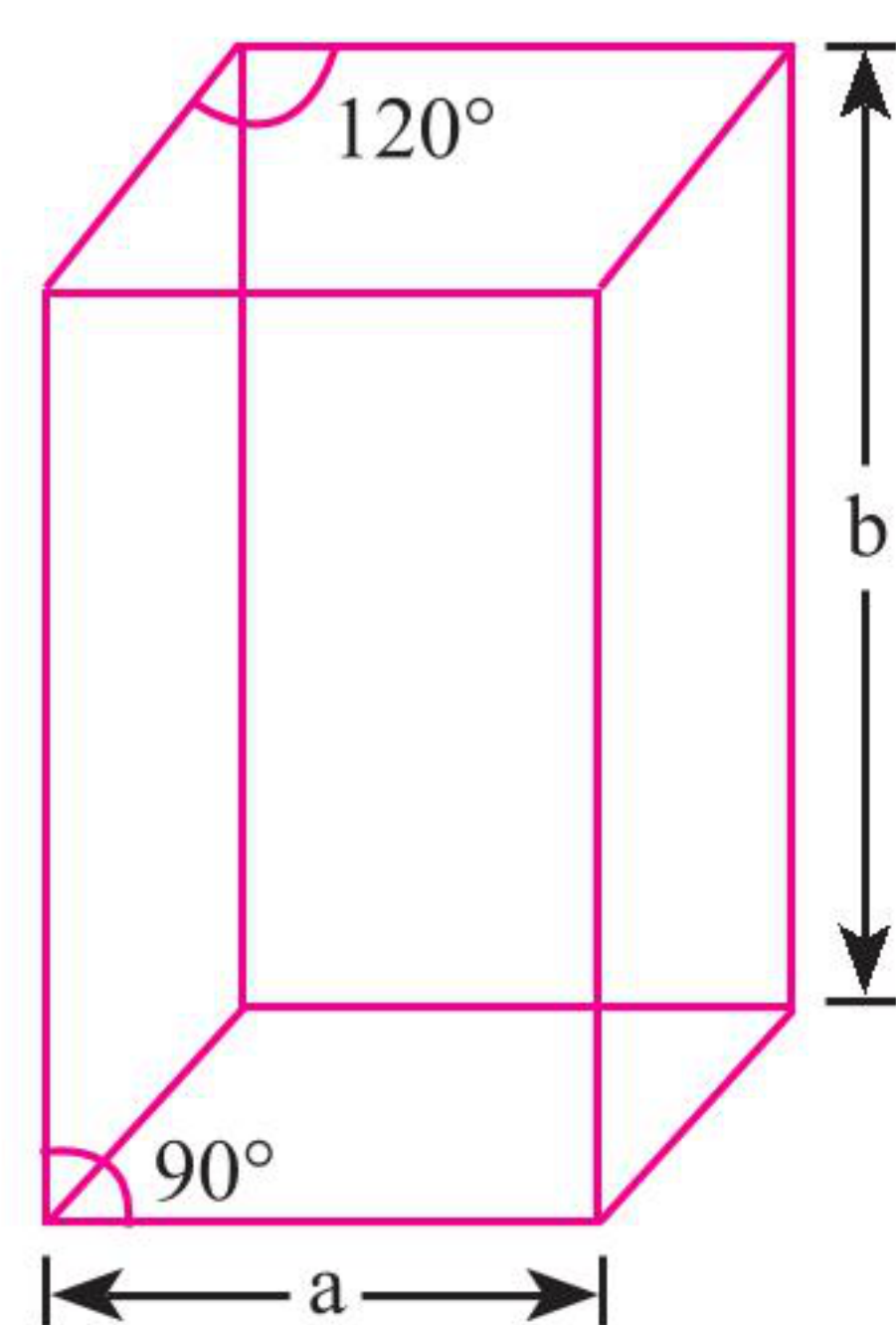
- | | | |
|---------------------------|--------------------|-----------|
| 1. $-\ln X \approx 4$ | 2. a. 8.5 b. 5% | 9. 3 |
| 10. 4 g cm^{-3} | 11. 2 | 12. 1.125 |

Exercises

Single Correct Answer Type

Classification of Solids and Their Properties

- Which one is called pseudo solid?
 - (1) CaF_2
 - (2) Glass
 - (3) NaCl
 - (4) All
- Solids which do not show the same physical properties in different direction are called:
 - (1) Pseudo solids
 - (2) Isotropic solids
 - (3) Polymorphic solids
 - (4) Anisotropic solids
- Graphite is an example of :
 - (1) Ionic solid
 - (2) Covalent solid
 - (3) Metallic crystal
 - (4) None of these
- Amorphous solids are:
 - (1) Isotropic and supercooled liquids
 - (2) Anisotropic and supercooled liquids
 - (3) Isoenthalpic and superheated liquids
 - (4) Isotropic and superheated solids
- Crystals which are good conductor of electricity and heat are :
 - (1) Ionic crystals
 - (2) Covalent crystals
 - (3) Metallic crystals
 - (4) Molecular crystals
- Which of the crystal systems contains the maximum number of Bravais lattices?
 - (1) Cubic
 - (2) Hexagonal
 - (3) Triclinic
 - (4) Orthorhombic
- The most unsymmetrical and symmetrical systems are, respectively:
 - (1) Tetragonal, Cubic
 - (2) Triclinic, Cubic
 - (3) Rhombohedral, Hexagonal
 - (4) Orthorhombic, Cubic
- The crystal system of a compound with unit cell parameters, $a = 0.328 \text{ nm}$, $b = 0.328 \text{ nm}$, $c = 0.527 \text{ nm}$ and $\alpha = \beta = \gamma = 90^\circ$ is
 - (1) Cubic
 - (2) Tetragonal
 - (3) Monoclinic
 - (4) Rhombohedral
- What are the number of atoms per unit cell and the number of nearest neighbours in a simple cubic structures?
 - (1) 1, 6
 - (2) 4, 12
 - (3) 2, 8
 - (4) 2, 6
- What are the number of atoms per unit cell and the number of nearest neighbours in a face centered cubic structures?
 - (1) 4, 8
 - (2) 2, 8
 - (3) 2, 6
 - (4) 4, 12
- What are the number of atoms per unit cell and the number of nearest neighbours in a body centered cubic structures?
 - (1) 4, 12
 - (2) 1, 6
 - (3) 2, 8
 - (4) 2, 5
- Which of the following layering pattern will have a void fraction of 0.260?
 - (1) ABCCBAABC
 - (2) ABBAABBA
 - (3) ABCABCABC
 - (4) ABCAABCA
- If the ratio of coordination no. of A to that of B is $x : y$, then the ratio of no. of atoms of A to that no. of atoms of B in unit cell is:
 - (1) $x : y$
 - (2) $y : x$
 - (3) $x^2 : y$
 - (4) $y : x^2$
- When heated above 916°C , iron changes its bcc crystalline form to fcc without the change in the radius of atom. The ratio of density of the crystal before heating and after heating is:
 - (1) 1.069
 - (2) 0.918
 - (3) 0.725
 - (4) 1.231
- $\text{TiAl}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ is bcc with ' a ' = 1.22 nm. If the density of the solid is 2.32 g/cc, then the value of x is (Given: $N_A = 6 \times 10^{23}$; at. mass: $\text{Ti} = 204$, $\text{Al} = 27$, $\text{S} = 32$).
 - (1) 2
 - (2) 4
 - (3) 47
 - (4) 70
- A body centered cubic lattice is made up of hollow spheres of B . Spheres of solid A are present in hollow spheres of B . Radius of A is half of radius of B . What is the ratio of total volume of spheres of B unoccupied by A in a unit cell and volume of unit cell?
 - (1) $\frac{7\sqrt{3}\pi}{64}$
 - (2) $\frac{7\sqrt{3}}{128}$
 - (3) $\frac{7\pi}{24}$
 - (4) $\frac{7\pi\sqrt{3}}{64}$
- First three nearest neighbour distances for primitive cubic lattice are respectively (edge length of unit cell = a):
 - (1) $a, \sqrt{2}a, \sqrt{3}a$
 - (2) $\sqrt{3}a, \sqrt{2}a, a$
 - (3) $a, \sqrt{2}a, 2a$
 - (4) $a, \sqrt{3}a, 2a$
- First three nearest neighbour distances for body centered cubic lattice are respectively:
 - (1) $\sqrt{2}a, a, \sqrt{3}a$
 - (2) $\frac{a}{\sqrt{2}}, a, \sqrt{3}a$
 - (3) $\frac{\sqrt{3}a}{2}, a, \sqrt{2}a$
 - (4) $\frac{\sqrt{3}a}{2}, a, \sqrt{3}a$
- In a planar tetra-atomic molecule, XY_3 , X is at the centroid of the equilateral triangle formed by the atoms, Y . If the $X-Y$ bond distance is 1 Å, what is the distance between the centres of any two Y atoms?
 - (1) $1/\sqrt{3} \text{ Å}$
 - (2) $\sqrt{2} \text{ Å}$
 - (3) $\sqrt{3} \text{ Å}$
 - (4) $1/\sqrt{2} \text{ Å}$
- A_2B molecules (molar mass = 259.8 g/mol) crystallises in a hexagonal lattice as shown in figure. The lattice constants are $a = 5 \text{ Å}$ and $b = 8 \text{ Å}$. If density of crystal is 5 g/cm^3 then how many molecules are contained in given unit cell? (use $N_A = 6 \times 10^{23}$)
 - (1) 4, 12
 - (2) 1, 6
 - (3) 2, 8
 - (4) 2, 5



- (1) 6 (2) 4
(3) 4 (4) 2

21. Graphite has h.c.p arrangements of carbon atoms and the parallel planes are 3.55 Å apart. Determine density of graphite :

- (1) 2.46 g/cc (2) 0.41 g/cc
(3) 1 g/cc (4) 1.41 g/cc

22. Select right expression for determining packing fraction (P.F.) of NaCl unit cell (assume ideal) if ions along an edge diagonal are absent :

(Given: volume of unit cell = $16\sqrt{2} r_{\ominus}^3$)

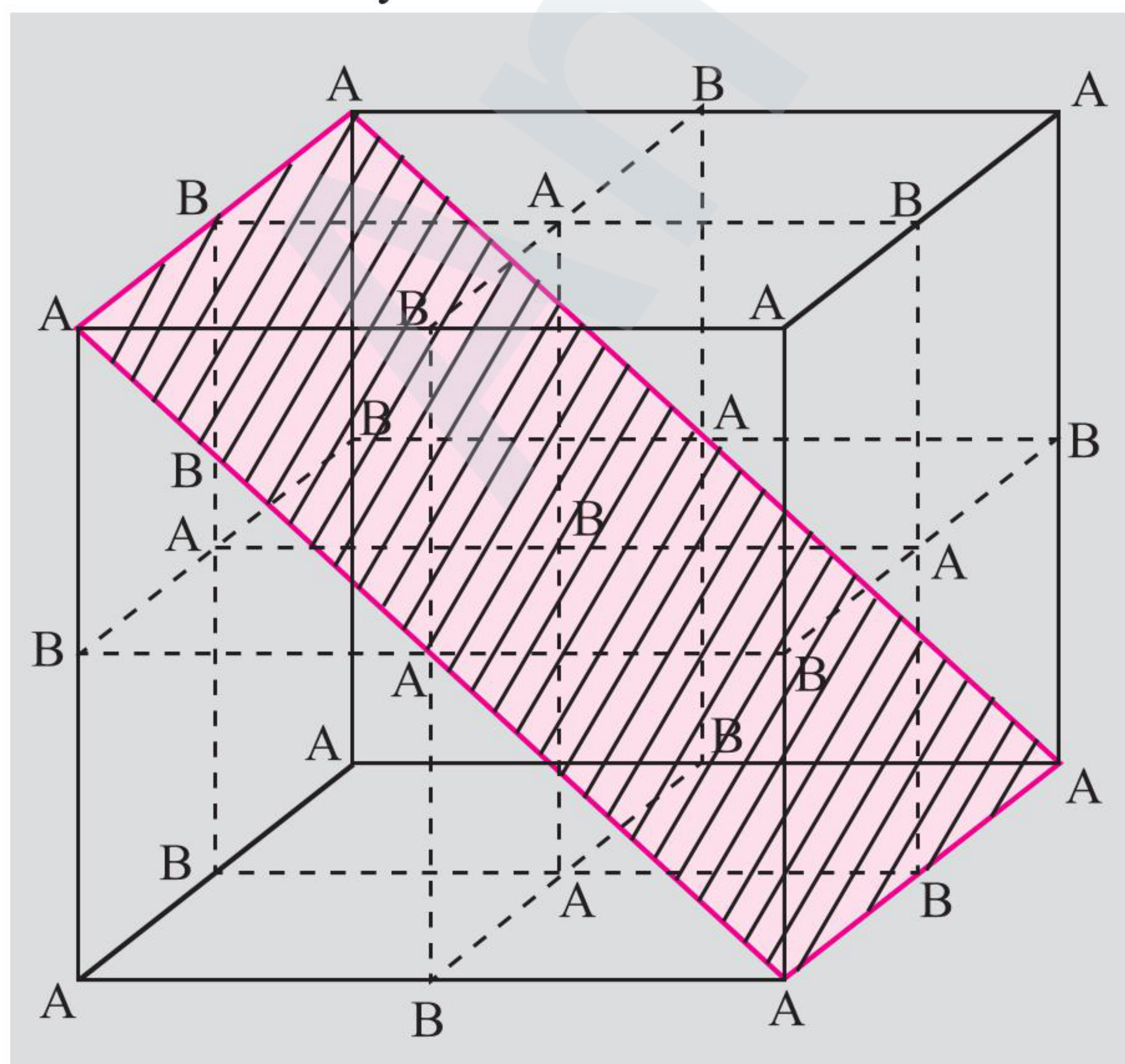
(1) $P.F. = \frac{\frac{4}{3}\pi(r_{\oplus}^3 + r_{\ominus}^3)}{16\sqrt{2} r_{\ominus}^3}$ (2) $P.F. = \frac{\frac{4}{3}\pi\left(\frac{5}{2}r_{\oplus}^3 + 4r_{\ominus}^3\right)}{16\sqrt{2} r_{\ominus}^3}$

(3) $P.F. = \frac{\frac{4}{3}\pi\left(\frac{5}{2}r_{\oplus}^3 + r_{\ominus}^3\right)}{16\sqrt{2} r_{\ominus}^3}$ (4) $P.F. = \frac{\frac{4}{3}\pi\left(\frac{7}{2}r_{\oplus}^3 + r_{\ominus}^3\right)}{16\sqrt{2} r_{\ominus}^3}$

23. A crystal is made of particles X, Y and Z. X forms fcc packing. Y occupies all the octahedral voids of X and Z occupies all the tetrahedral voids of X. If all the particles along one body diagonal are removed then the formula of the crystal would be:

- (1) XYZ_2 (2) X_2YZ_2
(3) $X_8Y_4Z_5$ (4) $X_5Y_4Z_8$

24. A crystal is made of particles A and B. A forms fcc packing and B occupies all the octahedral voids. If all the particles along the plane as shown in figure are removed, then, the formula of the crystal would be:



- (1) AB (2) A_5B_7
(3) A_7B_5 (4) None of these

25. Given length of side of hexagonal unit cell is $\frac{100}{\sqrt{2}}$ pm. The volume of hexagonal unit cell is (in pm^3):

- (1) 8×10^6 (2) 1.5×10^6
(3) 64×10^6 (4) 36×10^6

26. A crystal may have one or more planes and one or more axes of symmetry but it possesses:

- (1) Two centres of symmetry
(2) One centre of symmetry
(3) No centre of symmetry
(4) None of the above

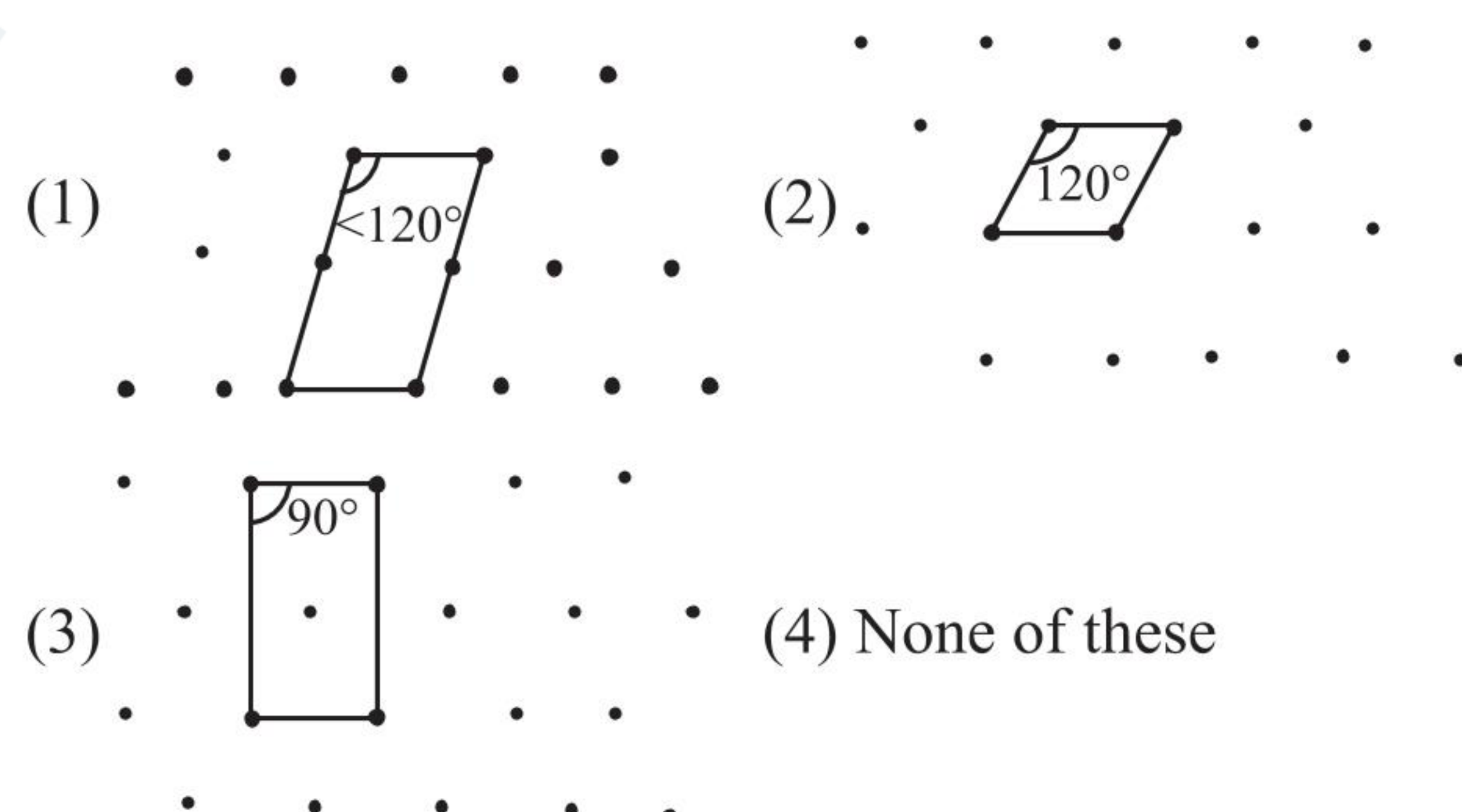
27. TiO_2 is well known example of:

- (1) Triclinic system (2) Tetragonal system
(3) Monoclinic system (4) None of these

28. The crystals are bounded by plane faces (f), straight edges (e) and interfacial angle (c). The relationship between these is:

- (1) $f + c = e + 2$ (2) $f + e = c + 2$
(3) $c + e = f + 2$ (4) None of these

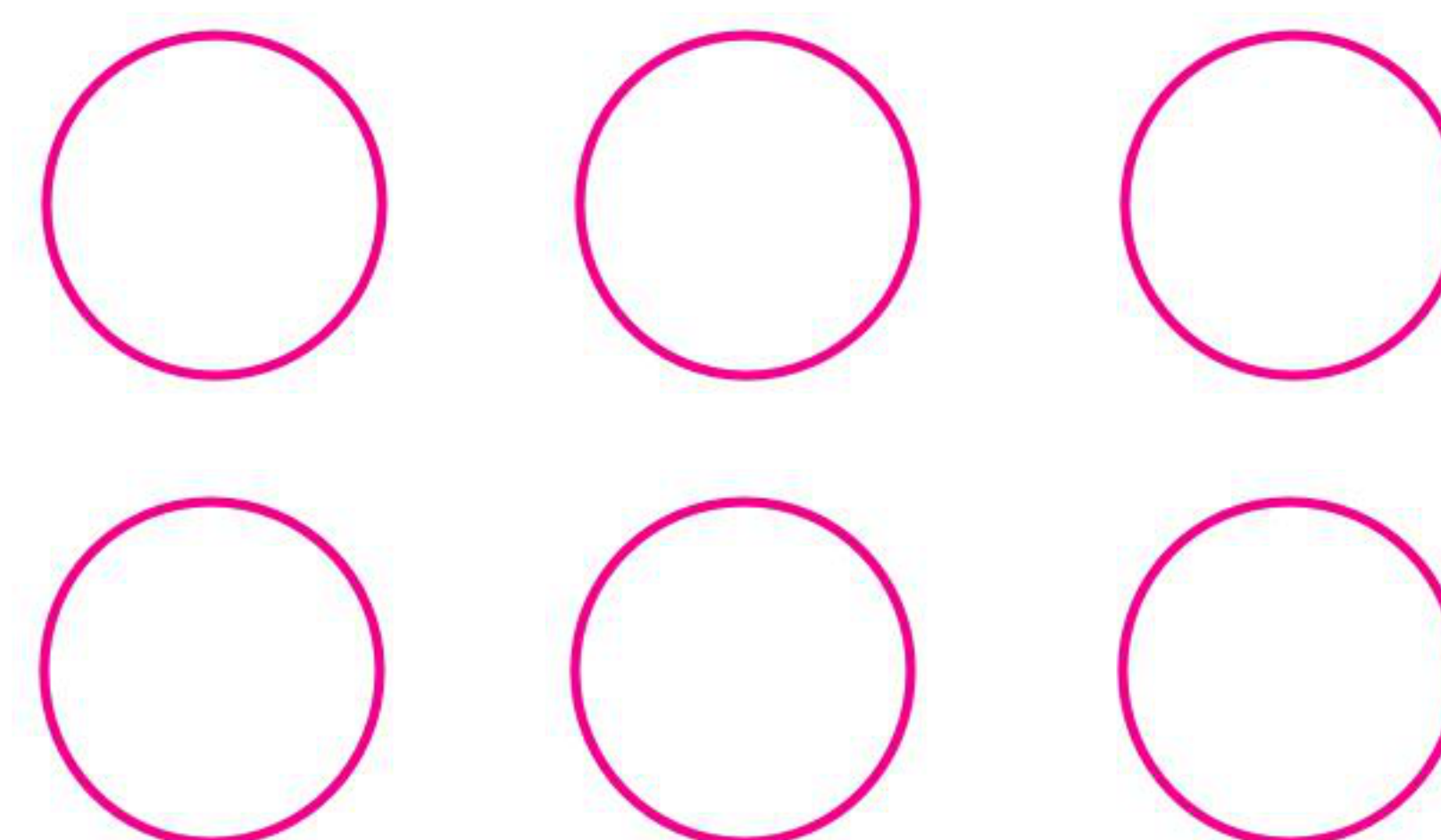
29. Ice molecules can exhibit up to sixteen different phases that depend on temperature and pressure. Which of the following diagram represents the location of lattice points within the space lattice of ice

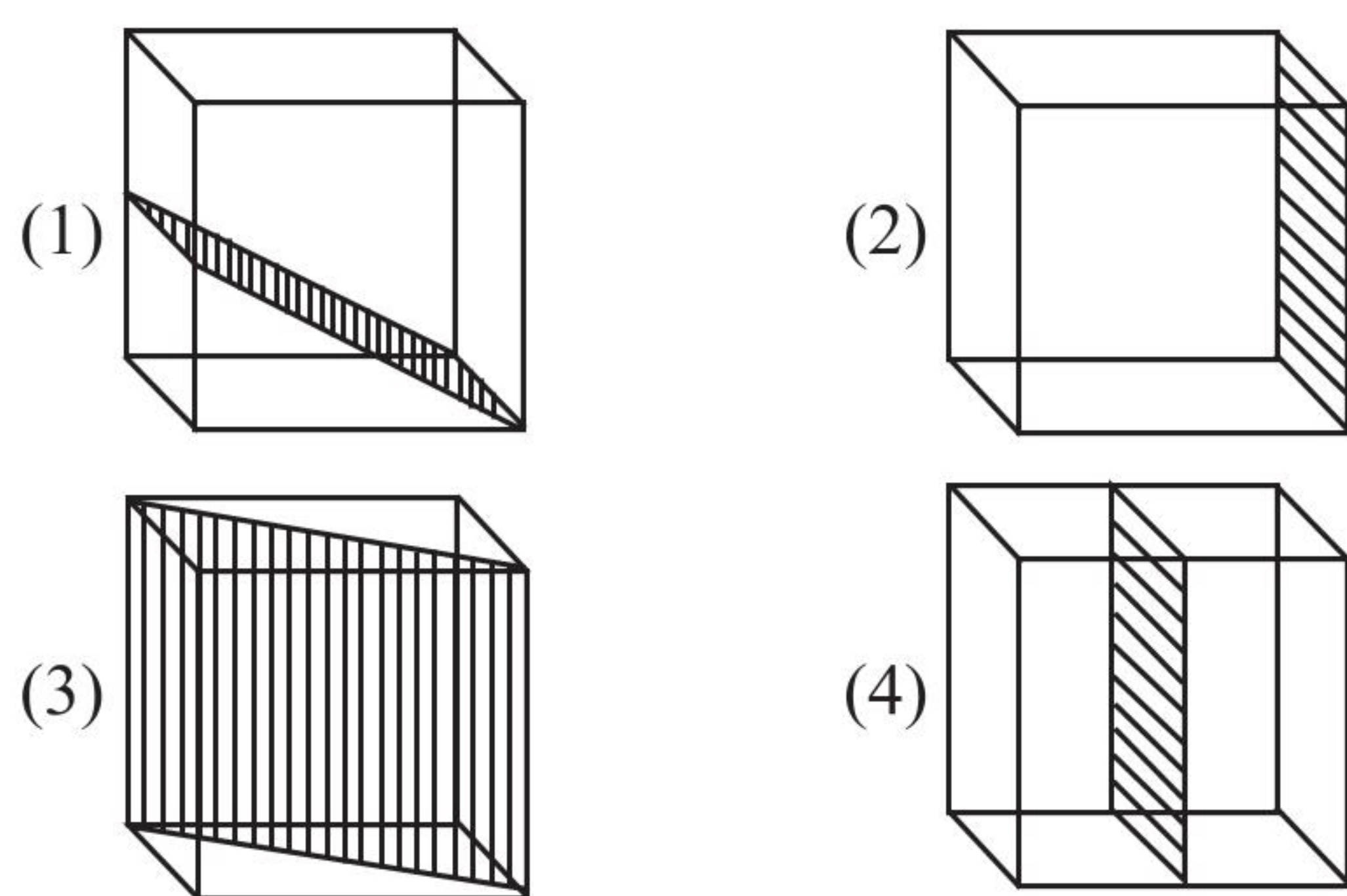


30. Liquid H_2O is densest, essentially 1.00 g/cm^3 , at 4°C and becomes less dense as the water molecules begin to form crystals ice as the freezing point is reached. Ice is 83 % less dense than liquid water the structure of ice is:

- (1) Cubic (2) Hexagonal
(3) Orthorhombic (4) Rhombohedral

31. Which of the following shaded plane in fcc lattice contains arrangement of atoms as shown below:





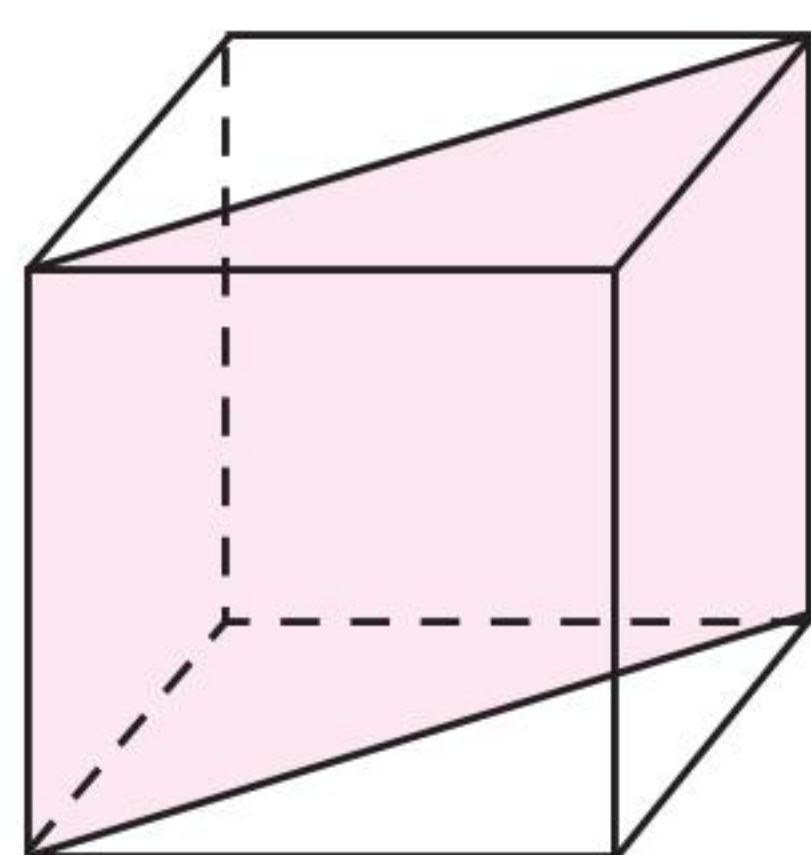
32. A metal crystallises in bcc lattice. The % fraction of edge length not covered by atom is:

- (1) 10.24 % (2) 13.4%
(3) 12.4 % (4) 11.4%

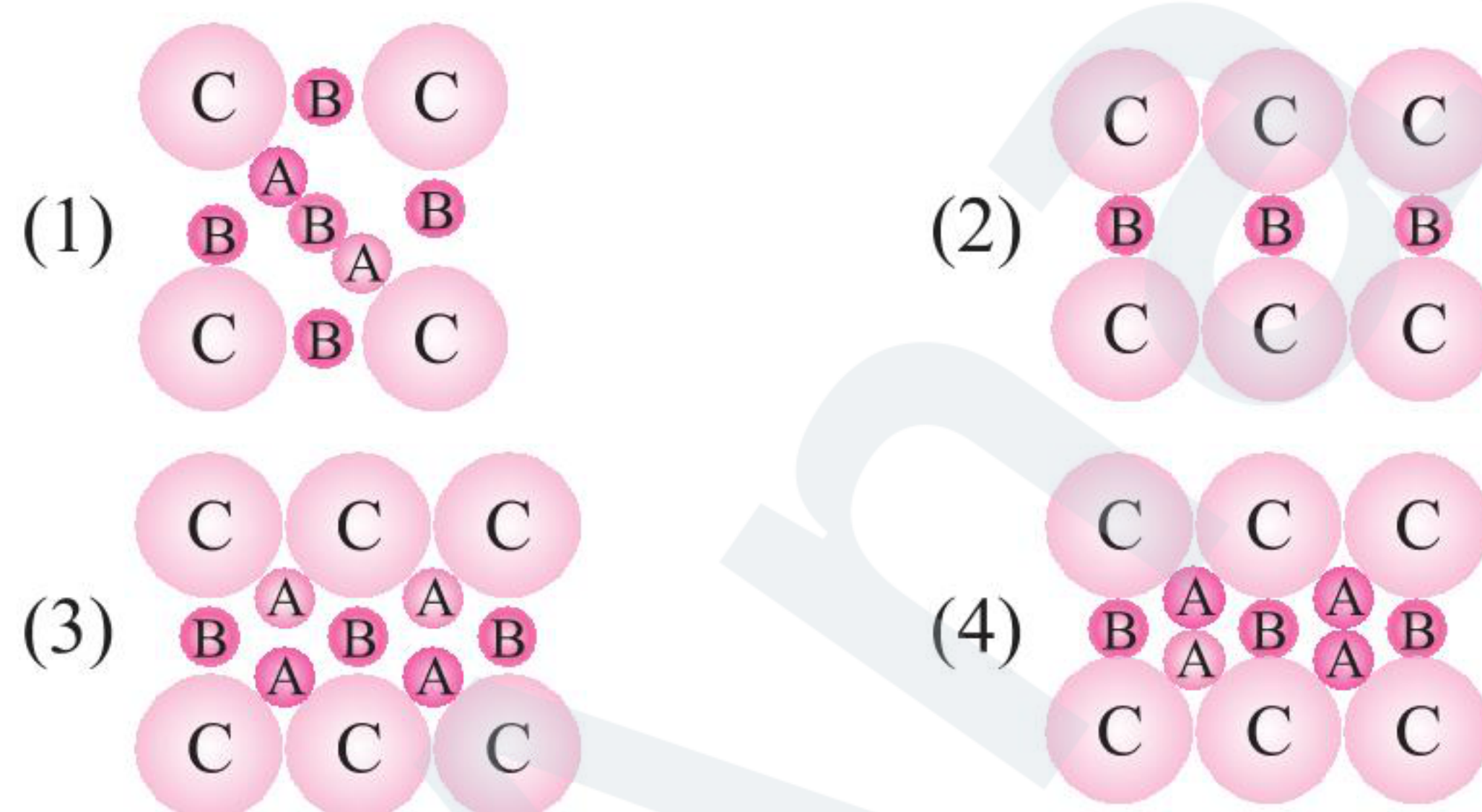
33. A crystal is made up of particles X, Y, and Z. X forms fcc packing. Y occupies all octahedral voids of X and Z occupies all tetrahedral voids of X. If all the particles along one body diagonal are removed, then the formula of the crystal would be

- (1) XYZ_2 (2) X_2YZ_2
(3) $X_8Y_4Z_5$ (4) $X_5Y_4Z_8$

34. In a hypothetical solid, C atoms are found to form cubical close-packed lattice. A atoms occupy all tetrahedral voids and B atoms occupy all octahedral voids.



A and B atoms are of appropriate size, so that there is no distortion in the ccp lattice of C atoms. Now if a plane as shown in the following figure is cut, then the cross section of this plane will look like



35. What is the maximum number of layers of atoms in close-packed planes that will lie within two imaginary parallel

planes having a distance between them of $13\sqrt{\frac{2}{3}}r$ (where

r is the radius of atom) in the copper crystal (fcc)?

(Consider the atoms to be within the parallel planes if their centres are on or within the two parallel planes).

- (1) 5 (2) 6
(3) 7 (4) 8

36. Analysis show that nickel oxide consists of nickel ion with 96% ions having d^8 configuration and 4% having d^7 configuration. Which amongst the following best represents the formula of the oxide?

- (1) $Ni_{1.02}O_{1.00}$ (2) $Ni_{0.96}O_{1.00}$
(3) $Ni_{0.98}O_{0.98}$ (4) $Ni_{0.98}O_{1.00}$

37. What is the density of Na_2O having antifluorite-type crystal structure, if the edge length of cube is 100 pm and what is the effect on density by 0.05% Frenkel defect?

- (1) 823.5 g cm^{-3} , density decreases
(2) 414.16 g cm^{-3} , density decreases
(3) 823.5 g cm^{-3} , density remains same
(4) 414.16 g cm^{-3} , density remains same

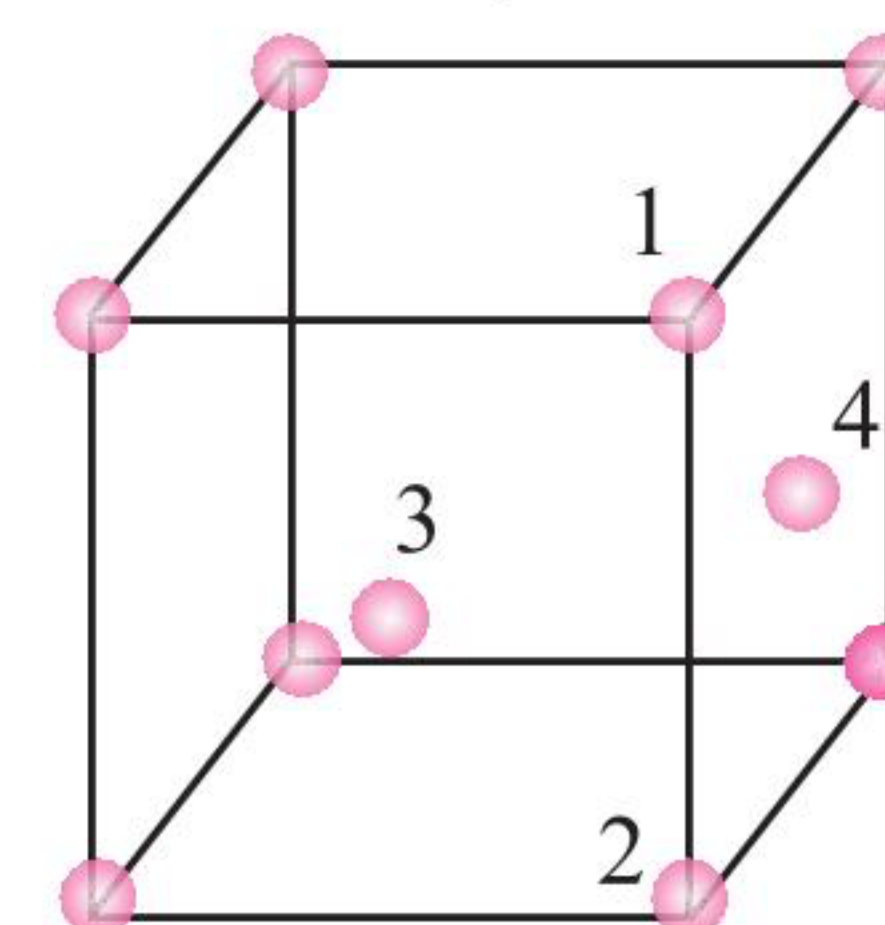
38. In the calcium fluoride structure, the coordination number of the cations and the anions are, respectively,

- (1) 6 and 6 (2) 8 and 4
(3) 4 and 4 (4) 4 and 8

39. A metallic crystal crystallizes into a lattice containing a sequence of layers ABABAB... . Any packing of spheres leaves out voids in the lattice. What percentage by volume of this lattice is empty space?

- (1) 74% (2) 26%
(3) 50% (4) None of these

40. In an fcc unit cell, atoms are numbered as shown below. The atoms not touching each other are (Atom numbered 3 is face centre of front face)

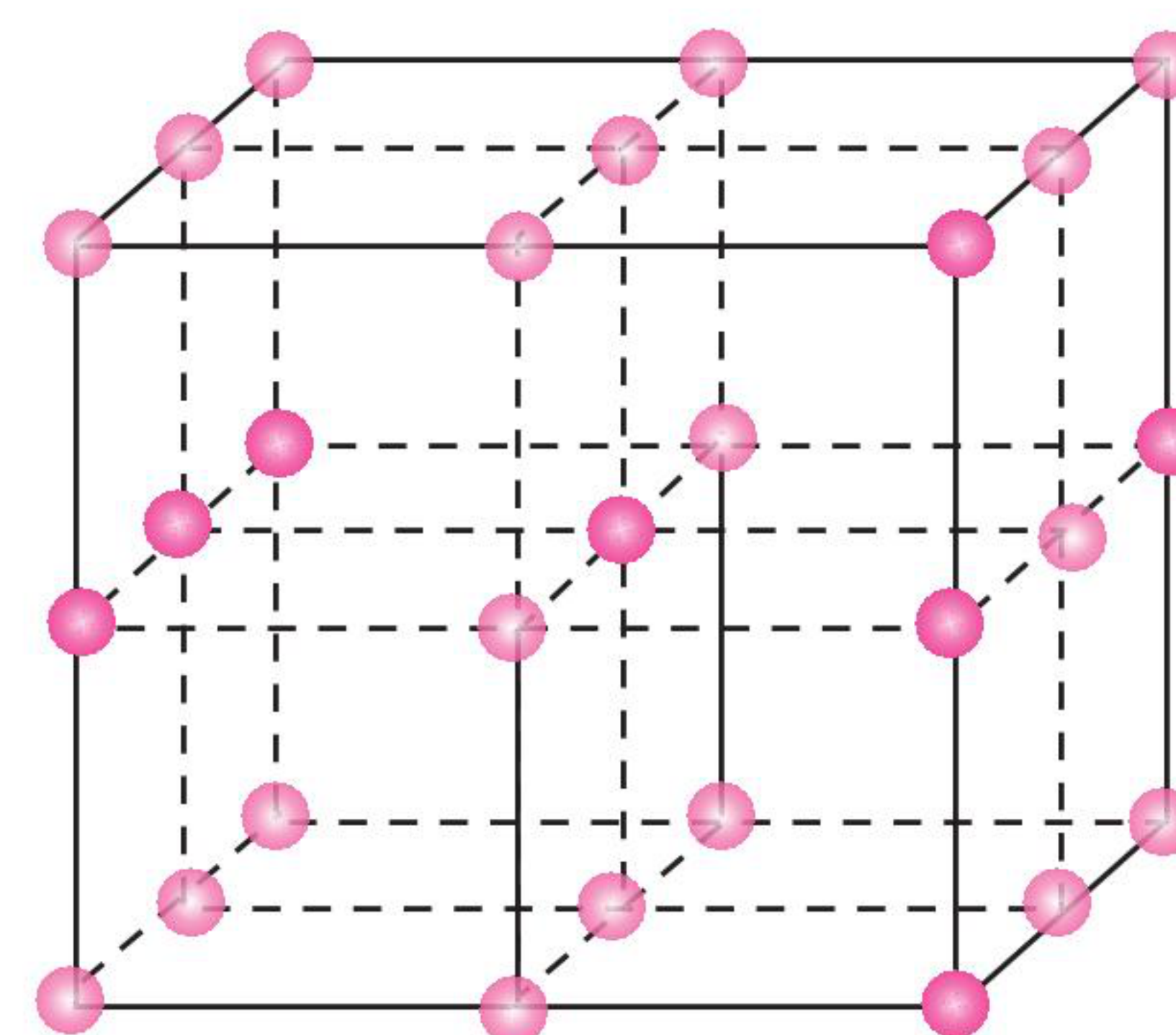


- (1) 3 and 4 (2) 1 and 3
(3) 1 and 2 (4) 2 and 4

41. The number of nearest neighbours and next nearest neighbours of an Na^+ ion in a crystal of NaCl are, respectively,

- (1) $6Na^+$, $12Cl^-$ (2) $6Cl^-$, $12Na^+$
(3) $12Cl^-$, $12Na^+$ (4) $6Cl^-$, $6Na^+$

42. The following diagram shows the arrangement of lattice points with $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$. Choose the correct options.



- (1) The arrangement is sc with each lattice point surrounded by 6 nearest neighbours.
 (2) The arrangement is sc with each lattice point surrounded by 8 nearest neighbours.
 (3) The arrangement is fcc with each lattice point surrounded by 12 nearest neighbours.
 (4) The arrangement is bcc with each lattice point surrounded by 8 nearest neighbours.
43. The number of atoms in 100 g of an fcc crystal with density = 10.0 g cm^{-3} and cell edge equal to 200 pm is equal to
 (1) 5×10^{24} (2) 5×10^{25}
 (3) 6×10^{23} (4) 2×10^{25}
44. In a tetragonal crystal
 (1) $a = b = c$, $\alpha = \beta = 90^\circ \neq \gamma$
 (2) $\alpha = \beta = \gamma = 90^\circ$, $a = b \neq c$
 (3) $\alpha = \beta = \gamma = 90^\circ$, $a \neq b \neq c$
 (4) $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $a = b \neq c$
45. If the lattice parameter of Si = $5.43 \text{ \AA}$ and the mass of Si atom is $28.08 \times 1.66 \times 10^{-27} \text{ kg}$, the density of silicon in kg m^{-3} is (Given: Silicon has diamond cubic structure)
 (1) 2330 (2) 1115
 (3) 3445 (4) 1673
46. The lattice parameter of GaAs (radius of Ga = $1.22 \text{ \AA}$, As = $1.25 \text{ \AA}$) is
 (1) $5.635 \text{ \AA}$ (2) $2.852 \text{ \AA}$
 (3) $5.774 \text{ \AA}$ (4) $4.94 \text{ \AA}$
47. In cubic ZnS (II–VI) compounds, if the radii of Zn and S atoms are $0.74 \text{ \AA}$ and $1.70 \text{ \AA}$, the lattice parameter of cubic ZnS is
 (1) $11.87 \text{ \AA}$ (2) $5.634 \text{ \AA}$
 (3) $5.14 \text{ \AA}$ (4) $2.97 \text{ \AA}$
48. Na and Mg crystallize in bcc- and fcc-type crystals, the ratio of number of atoms present in the unit cell of their respective crystal is
 (1) 1 (2) 0.5
 (3) 3 (4) 4
49. An ionic solid $A^{\oplus}B^{\ominus}$ crystallizes as a bcc structure. The distance between cation and anion in the lattice is 338 pm. The edge length of cell is
 (1) 338 pm (2) 390.3 pm
 (3) 292.7 pm (4) 507 pm
50. An ionic solid $A^{\oplus}B^{\ominus}$ crystallizes as an fcc structure. If the edge length of cell is 508 pm and the radius of anion is 144 pm, the radius of cation is
 (1) 110 pm (2) 364 pm
 (3) 220 pm (4) 288 pm
51. The γ -form of iron has fcc structure (edge length 386 pm) and β -form has bcc structure (edge length 290 pm). The ratio of density in γ -form and β -form is
 (1) 0.9788 (2) 1.02
 (3) 1.57 (4) 0.6344
52. The density of an ionic compound ($M_w = 58.5$) is 2.165 kg m^{-3} and the edge length of unit cell is 562 pm, then the closest distance between $A^{\oplus}B^{\ominus}$ and Z_{eff} of unit cell is
 (1) 281 pm, 4 (2) 562 pm, 2
 (3) 562 pm, 4 (4) 281 pm, 2
53. The edge length of unit cell of a metal ($M_w = 24$) having cubic structure is $4.53 \text{ \AA}$. If the density of metal is 1.74 g cm^{-3} , the radius of metal is ($N_A = 6 \times 10^{23}$)
 (1) 180 pm (2) 160 pm
 (3) 140 pm (4) 190 pm
54. The ratio of packing density in fcc, bcc, and cubic structure is, respectively,
 (1) 1: 0.92 : 0.70 (2) 0.70 : 0.92 : 1
 (3) 1 : 0.70 : 0.92 (4) 0.92 : 0.70 : 1
55. How many unit cells are present in a cubic-shaped ideal crystal of NaCl of mass 1.0 g?
 (1) 1.28×10^{21} (2) 1.71×10^{21}
 (3) 2.57×10^{21} (4) 5.14×10^{21}
56. The volume of atoms present in a face-centred cubic unit cell of a metal (r is atomic radius) is
 (1) $\frac{20}{3}\pi r^3$ (2) $8\pi r^3$
 (3) $4\pi r^3$ (4) $\frac{16}{3}\pi r^3$
57. An elemental crystal has a density of 8570 kg m^{-3} . The packing efficiency is 0.68. If the closest distance between neighbouring atoms is $2.86 \text{ \AA}$, the mass of one atom is ($1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$)
 (1) 186 amu (2) 93 amu
 (3) 46.5 amu (4) 43 amu
58. The atomic fraction (d) of tin in bronze (fcc) with a density of 7717 kg m^{-3} and a lattice parameter of $3.903 \text{ \AA}$ is ($A_w \text{ Cu} = 63.54$, $\text{Sn} = 118.7$, $1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$)
 (1) 0.01 (2) 0.05
 (3) 0.10 (4) 3.8
59. A metal of density $7.5 \times 10^3 \text{ kg m}^{-3}$ has an fcc crystal structure with lattice parameter $a = 400 \text{ pm}$. Calculate the number of unit cells present in 0.015 kg of the metal.
 (1) 6.250×10^{22} (2) 3.125×10^{23}
 (3) 3.125×10^{22} (4) 1.563×10^{22}
60. The ratio of the volume of a tetragonal lattice unit cell to that of a hexagonal lattice unit cell is (both having same respective lengths)
 (1) $\frac{\sqrt{3}}{2} abc$ (2) $\frac{2}{3\sqrt{3}}$
 (3) $\frac{2}{\sqrt{3}} \frac{a^2 c}{b}$ (4) 1

61. An fcc lattice has a lattice parameter $a = 400$ pm. Calculate the molar volume of the lattice including all the empty space.

(1) 10.8 mL (2) 96 mL
(3) 8.6 mL (4) 9.6 mL

62. A metal crystallizes in bcc lattice. The percent fraction of edge length not covered by atom is

(1) 10.4% (2) 13.4%
(3) 12.4% (4) 11.4%

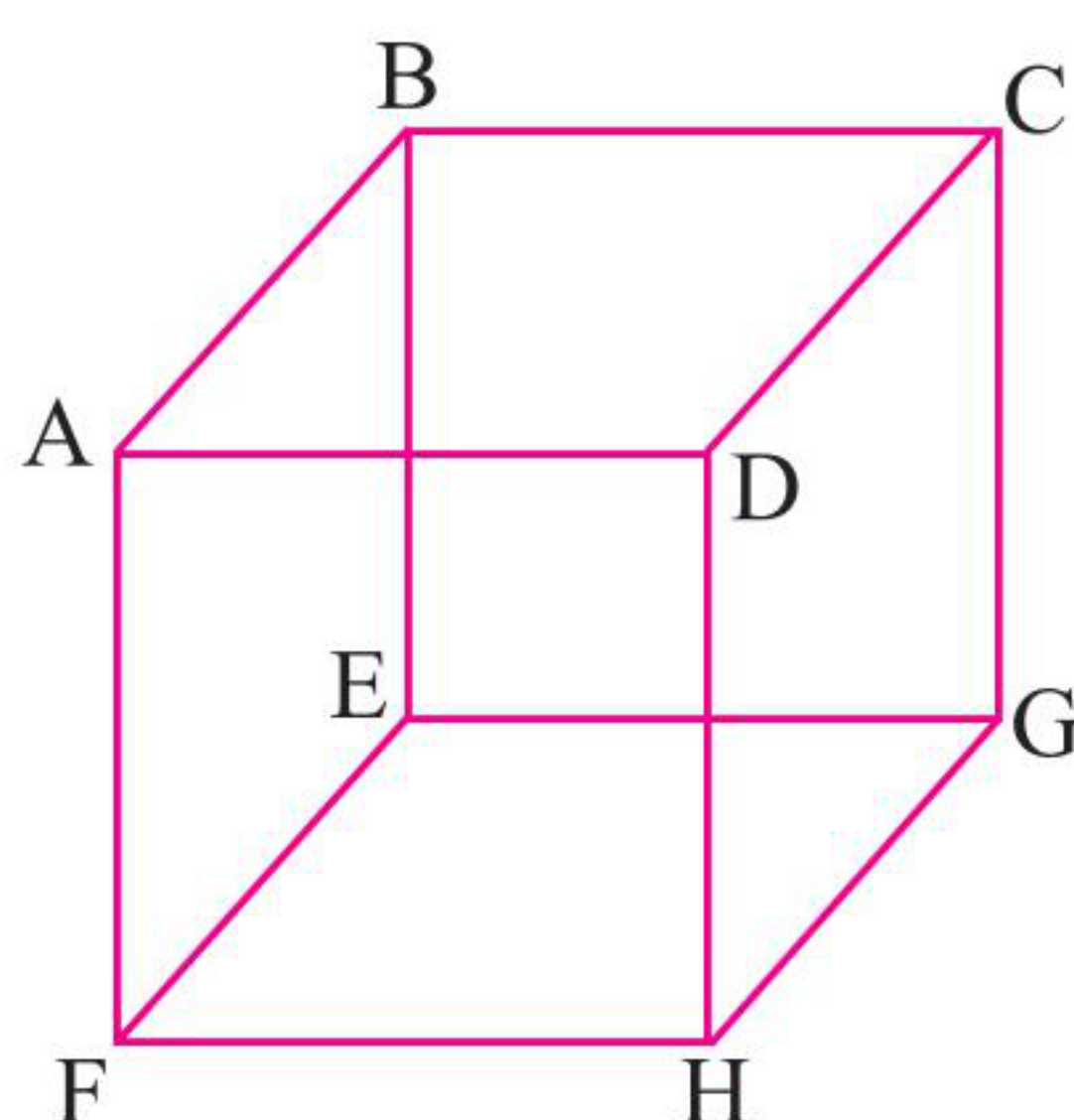
63. In the cubic lattice given below, the three distances between the atoms A–B, A–C, and A–G are, respectively,

(1) $a, \sqrt{2}a, \sqrt{3}a$

(2) $a, \sqrt{3}a, \sqrt{2}a$

(3) $\frac{a}{2}, \frac{a}{\sqrt{2}}, \frac{\sqrt{3}a}{2}$

(4) $a, \frac{\sqrt{3}a}{2}, \sqrt{2}a$



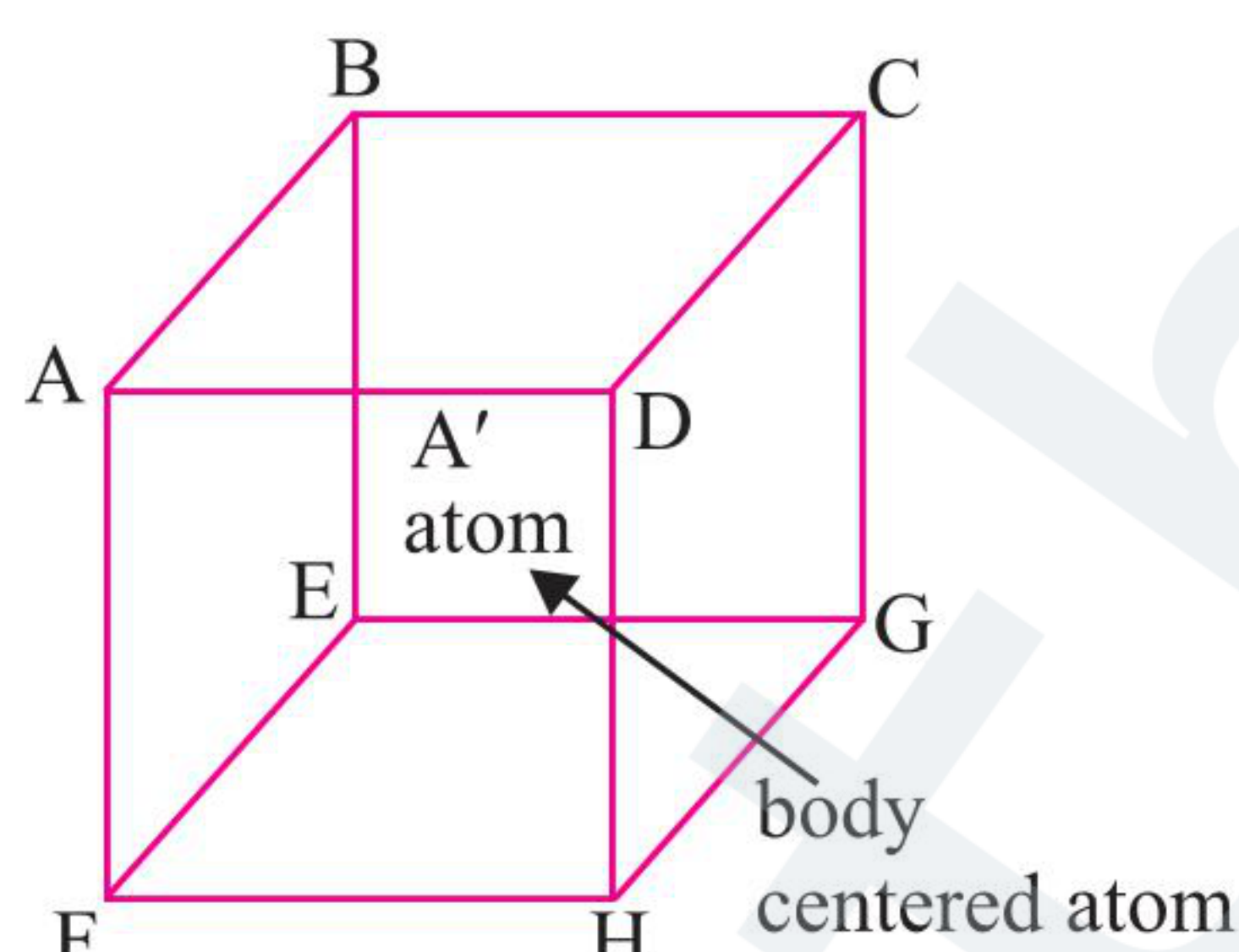
64. In body-centred cubic lattice given below, the three distances AB, AC, and AA' are

(1) $a, \sqrt{2}a, \frac{\sqrt{3}a}{2}$

(2) $a, \frac{\sqrt{3}a}{2}, \sqrt{2}a$

(3) $\frac{\sqrt{3}a}{2}, \sqrt{2}a, a$

(4) $a, \frac{a}{\sqrt{2}}, \frac{\sqrt{3}a}{2}$



65. Two ionic solids AB and CB crystallize in the same lattice. If r_{A^+}/r_{B^-} and r_{C^+}/r_{B^-} are 0.50 and 0.70, respectively, then the ratio of edge length of AB and CD is

(1) 0.68 (2) 0.78
(3) 0.88 (4) 0.98

66. A molecule A_2B ($M_w = 166.4$) occupies triclinic lattice with $a = 5$ Å, $b = 8$ Å, and $c = 4$ Å. If the density of AB_2 is 5.2 g cm $^{-3}$, the number of molecules present in one unit cell is

(1) 2 (2) 3
(3) 4 (4) 5

67. Na and Mg crystallize in bcc- and fcc-type crystals, respectively, then the number of atoms of Na and Mg present in the unit cell of their respective crystal is

(1) 4 and 2 (2) 9 and 14
(3) 14 and 9 (4) 2 and 4

68. A solid has a structure in which W atoms are located at the corners of a cubic lattice, O atoms at the centre of edges, and Na atom at the centre of the cube. The formula for the compound is

(1) $NaWO_2$ (2) $NaWO_3$
(3) Na_2WO_3 (4) $NaWO_4$

69. The intermetallic compound LiAg crystallizes in cubic lattice in which both lithium and silver have coordination number of 8. The crystal class is

(1) Simple cubic (2) Body-centred cubic
(3) Face-centred cubic (4) None of these

70. The edge length of a face-centred cubic unit cell is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is

(1) 144 pm (2) 288 pm
(3) 618 pm (4) 398 pm

71. In the crystals of which of the following ionic compounds would you expect maximum distance between the centres of the cations and anions?

(1) LiF (2) CsF
(3) CsI (4) LiI

72. How many kinds of space lattices are possible in a crystal?

(1) 23 (2) 7
(3) 230 (4) 14

73. Potassium crystallizes with a

(1) Face-centred cubic lattice
(2) Body-centred cubic lattice
(3) Simple cubic lattice
(4) Orthorhombic lattice

74. A compound formed by elements A and B crystallizes in the cubic structure where B atoms are at the face-centres. The formula of the compound is

(1) AB_3 (2) AB
(3) A_3B (4) A_2B_2

75. The number of unit cells in 58.5 g of NaCl is nearly

(1) 6×10^{20} (2) 3×10^{22}
(3) 1.5×10^{23} (4) 0.5×10^{24}

76. The packing fraction for a body-centred cube is

(1) 0.42 (2) 0.53
(3) 0.68 (4) 0.82

77. In NaCl, the chloride ions occupy the space in a fashion of

(1) fcc (2) bcc
(3) Both (4) None

78. The range of radius ratio (cationic to anionic) for an octahedral arrangement of ions in an ionic solid is

(1) 0.155–0.225 (2) 0.225–0.414
(3) 0.414–0.732 (4) 0.732–1.000

79. When molten zinc is cooled to solid state, it assumes hcp structure. Then the number of nearest neighbours of zinc atom will be

(1) 4 (2) 6
(3) 8 (4) 12

80. The interionic distance for cesium chloride crystal will be

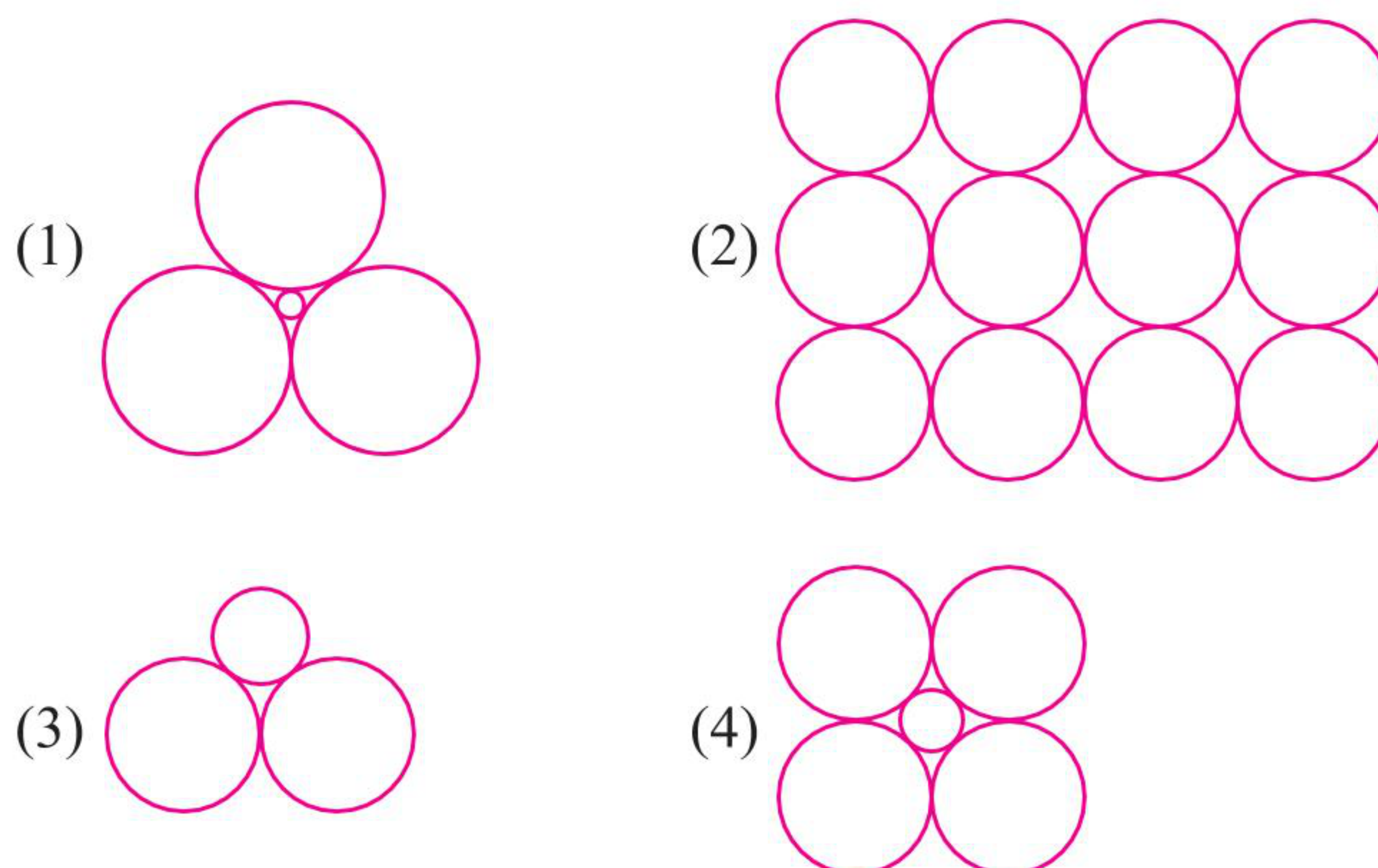
(1) a (2) $a/2$
(3) $\sqrt{3}a/2$ (4) $2a/\sqrt{3}$

81. In the structure of diamond, carbon atoms appear at
 (1) 0, 0, 0, and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ (2) $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$, and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
 (3) 0, 0, 0, and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ (4) 0, 0, 0, and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$
82. Which of following statements is correct in the zinc-blende-type structure of an ionic compound?
 (1) Coordination number of each cation and anion is 2.
 (2) Coordination number of each cation and union is 4.
 (3) Coordination number of each cation and union is 6.
 (4) Coordination number of each cation and union is 8.
83. In a body-centred cubic unit cell of closest packed atoms, the radius of atom in terms of edge length a of the unit cells is
 (1) $a/2$ (2) $a/\sqrt{2}$
 (3) $a/2\sqrt{2}$ (4) $\sqrt{3}a/4$
84. Which of the following expressions is correct in the case of a sodium chloride unit cell (edge length, a)?
 (1) $r_{\oplus} + r_{\ominus} = a$ (2) $r_{\oplus} + r_{\ominus} = a/2$
 (3) $r_{\oplus} + r_{\ominus} = 2a$ (4) $r_{\oplus} + r_{\ominus} = \sqrt{2}a$
85. In silicon crystal, Si atoms form fcc arrangement where 4 out of 8 TVs are also occupied by Si atoms. Z_{eff} of unit cell is
 (1) 1 (2) 2
 (3) 4 (4) 8
86. Which of the following crystal systems exist in bc, end-centred, fc, as well as primitive unit cell?
 (1) Hexagonal (2) Cubic
 (3) Triclinic (4) Orthorhombic
87. In a cubic unit cell, A atoms are present on alternative corners, B atoms are present on alternate faces, and C atoms are present on alternate edges and body centre of the cube. The simplest formula of the compound is
 (1) A_2BC_4 (2) AB_2C_4
 (3) ABC_4 (4) ABC_2
88. Which of the following statements is correct for the body-centred cubic structure of an ionic compound?
 (1) Coordination number of each cation and anion is 2.
 (2) Coordination number of each cation and anion is 4.
 (3) Coordination number of each cation and anion is 6.
 (4) Coordination number of each cation and anion is 8.
89. Aluminium metal has a density of 2.72 g cm^{-3} and crystallizes in a cubic lattice with an edge of 404 pm. Which of the following is correct?
 (1) It forms bcc unit cell
 (2) It forms fcc unit cell
 (3) Its CN = 8
 (4) Its CN is 6
90. ThO_2 exists in fluorite structure, what is the effective number of bivalent ion in the unit cell of ThO_2 ?
 (1) 2 (2) 4
 (3) 1 (4) 8
91. What is the coordination number of Th^{4+} in ThO_2 ?
 (1) 4 (2) 8
 (3) 6 (4) 12
92. The coordination number Cs and Br in CsBr are, respectively,
 (1) 8, 8 (2) 6, 6
 (3) 8, 6 (4) 6, 8
93. Fraction of total volume occupied by atoms in a simple cube is
 (1) $\sqrt{3}\pi/8$ (2) $\pi/6$
 (3) $\pi/3$ (4) $\sqrt{2}\pi/3$
94. Xenon crystallizes in fcc lattice and the edge of the unit cell is 620 pm, then the radius of Xe atom is
 (1) 219.20 pm (2) 438.5 pm
 (3) 290.3 pm (4) 318.53 pm
95. In BeO (zinc blende structure), Mg^{2+} is introduced in available TVs. The coordination numbers of Be^{2+} and Mg^{2+} are, respectively,
 (1) 8, 8 (2) 6, 6
 (3) 4, 4 (4) 8, 6
96. If the ions are removed from a single body diagonal in above case after doping, then the molecular formula of the unit cell would be
 (1) $\text{Mg}_2\text{Be}_{3.5}\text{O}_{2.5}$ (2) $\text{Mg}_3\text{Be}_3\text{O}_{3.75}$
 (3) $\text{Mg}_3\text{Be}_3\text{O}_{3.5}$ (4) $\text{Mg}_4\text{Be}_4\text{O}_{3.5}$
97. In spinel, Mg^{2+} is present in one-eighth of TVs in an fcc lattice of oxide ions and Al^{3+} ions are present in half of the OVs. The formula of spinel is
 (1) MgAl_3O_3 (2) MgAl_2O_3
 (3) MgAl_2O_4 (4) MgAl_3O_4

Tetrahedral and Octahedral voids

98. How many nearest neighbours are there in an atom or ion for an octahedral hole of a closed packed structure?
 (1) 4 (2) 6
 (3) 8 (4) 12
99. How many “nearest” and “next nearest” neighbours, respectively, does potassium have in bcc lattice?
 (1) 8, 8 (2) 8, 6
 (3) 6, 8 (4) 6, 6
100. The unit cell of diamond is made up of:
 (1) 6 carbon atoms 4 atoms constitute ccp and two atoms occupy half of octahedral voids
 (2) 8 carbon atom, 4 atoms constitute ccp and 4 atoms occupy all the octahedral voids
 (3) 8 carbon atoms, 4 atoms form fcc lattice and 4 atoms occupy half of the tetrahedral voids alternately

- (4) 12 carbon atoms, 4 atoms form fcc lattice and 8 atoms occupy all the tetrahedral holes
- 101.** In diamond, the coordination number of carbon is:
- Four and its unit cell has eight of carbon atoms
 - Four and its unit cell has six carbon atoms
 - Six and its unit cell has four carbon atoms
 - Four and its unit cell has four carbon atoms
- 102** In diamond, carbon atom occupy fcc lattice points as well as alternate tetrahedral voids. If edge length of the unit cell is 356 pm, then diameter of carbon atom is:
- 77.07 pm
 - 154.14 pm
 - 251.7 pm
 - 89 pm
- 103.** The distance between an octahedral and tetrahedral void in fcc lattice would be:
- $\sqrt{3}a$
 - $\frac{\sqrt{3}a}{2}$
 - $\frac{\sqrt{3}a}{3}$
 - $\frac{\sqrt{3}a}{4}$
- 104.** In the rock salt AB , of C introduced in tetrahedral voids such that no distortion occurs, then formula of resultant compound is:
- ABC
 - ABC_2
 - A_4B_4C
 - ABC_8
- 105.** How many tetrahedral holes are occupied in diamond?
- 25%
 - 50%
 - 75%
 - 100%
- 106.** Total number of voids in 0.5 mole of a compound forming hexagonal closed packed structure are
- 6.022×10^{23}
 - 3.011×10^{23}
 - 9.034×10^{23}
 - 4.516×10^{23}
- 107.** The melting point of RbBr is 682°C , while that of NaF is 988°C . The principal reason that melting point of NaF is much higher than that of RbBr is that :
- The two crystals are not isomorphous
 - The molar mass of NaF is smaller than that of RbBr
 - The internuclear distance $r_c + r_a$ is greater for RbBr than for NaF
 - The bond in RbBr has more covalent character than the bond in NaF
- 108.** Which of the crystals have same general formula ?
- Rock salt type and Anti-fluorite type
 - Rock salt type and Fluorite type
 - Fluorite type and CsCl type
 - Sphalerite type and Rock salt type A_4B_4 or AB .
- 109.** A non stoichiometric compound $\text{Cu}_{1.8}\text{S}$ is formed due to incorporation of Cu^{2+} ions in the lattice of cuprous sulphide. What percentage of Cu^{2+} ion in the total copper content is present in the compound?
- 88.88
 - 11.11
 - 99.8
 - 89.8
- 110.** In the closest packing of atoms
- The size of TV is greater than that of OV.
 - The size of TV is smaller than that of OV.
 - The size of TV is equal to that of OV.
 - The size of TV may be greater or smaller or equal to that of OV depending upon the size of atoms.
- 111.** In a closed packed structure of mixed oxides, the lattice is composed of mixed oxides ions. One-eighth of tetrahedral voids are occupied by divalent cations (A^{2+}) while one-half of octahedral voids are occupied by trivalent cations (B^{3+}). The formula of mixed oxide is
- A_2BO_3
 - AB_2O_3
 - A_2BO_4
 - AB_2O_4
- 112.** If R is the radius of the octahedral voids and r is the radius of the atom in close packing, then r/R is equal to
- 2.41
 - 4.76
 - 3.22
 - 9.1
- 113.** Every atom or ion that forms an fcc unit cell is surrounded by
- Six OVs and eight TVs.
 - Eight OVs and six TVs.
 - Six OVs and six TVs.
 - Eight OVs and four TVs.
- 114.** Consider the structure of CsCl (8 : 8 coordination). How many Cs^+ ions occupy the second nearest neighbour locations of a Cs^+ ion ?
- 8
 - 24
 - 6
 - 16
- 115.** A TV in fcc is formed by atoms at
- 3 corners + 1 face centre
 - 3 face centres + 1 corner
 - 2 face centres + 2 corners
 - 2 face centres + 1 corner + 1 body centre
- 116.** The number of octahedral sites per sphere in fcc structure is
- 8
 - 4
 - 2
 - 1
- 117.** Which of the following figures represents the cross section of an OV?



118. The fraction of octahedral voids filled by Al^{3+} ions in Al_2O_3 ($r_{\text{Al}^{3+}}/r_{\text{O}^{2-}} = 0.43$) is

- (1) 0.43 (2) 0.287
(3) 0.667 (4) 1

119. In the closest packing of atoms, there are

- (1) One tetrahedral void and two octahedral voids per atom
(2) Two tetrahedral voids and one octahedral void per atom
(3) Two of each tetrahedral and octahedral voids per atom
(4) One of each tetrahedral and octahedral void per atom

120. If atoms are removed from half of the edge-centred OVs in RbBr , then the molecular formula of unit cell is

- (1) Rb_2Br_2 (2) $\text{Rb}_{1.5}\text{Br}_3$
(3) $\text{Rb}_{2.5}\text{Br}_4$ (4) $\text{Rb}_4\text{Br}_{2.5}$

Defects in Crystals

121. Transition metals, when they form interstitial compounds, the non-metals (H, B, C, N) are accommodated in:

- (1) Voids or holes in cubic-packed structure
(2) Tetrahedral voids
(3) Octahedral voids
(4) All of these

122. In diamond, each carbon atom is bonded to four other carbon atoms tetrahedrally. Alternate tetrahedral voids are occupied by carbon atoms. The number of carbon atoms per unit cell is:

- (1) 4 (2) 6
(3) 8 (4) 12

123. If an element (at. mass = 50) crystallises in fcc lattice, with $a = 0.50$ nm. What is the density of unit cell if it contains 0.25% Schottky defects (use $N_A = 6 \times 10^{23}$)?

- (1) 2.0 g/cc (2) 2.66 g/cc
(3) 3.06 g/cc (4) None of these

124. When light strikes a photographic (AgBr) paper, silver atoms move in through these defects to:

- (1) Form -ve images
(2) Form tiny clumps of silver atoms
(3) Form a colour image
(4) None of the above

125. If we mix a pentavalent impurity in a crystal lattice of germanium, what type of semiconductor formation will occur?

- (1) *p*-type (2) *n*-type
(3) Both (1) and (2) (4) None of these

126. Which of the following statements are true?

- (1) Piezo-electricity is due to net dipole moment
(2) Ferro-electricity is due to alignment of dipoles in same direction
(3) Pyro-electricity is due to heating polar crystals
(4) All of the above

127. At what angles for the first order diffraction, spacing between two planes respectively are λ and $\frac{\lambda}{2}$

- (1) $0^\circ, 90^\circ$ (2) $90^\circ, 0^\circ$
(3) $30^\circ, 90^\circ$ (4) $90^\circ, 30^\circ$

128. Levitation is achieved by

- (1) Mutual repulsion between permanent magnet and a superconductor
(2) Mutual repulsion between a weak magnet and a superconductor
(3) A slight attraction between a permanent magnet and a superconductor
(4) None of these

129. Which one possesses perovskite structure?

- (1) BaTiO_4 (2) NaMgF_3
(3) BaTiO_2 (4) NaMg_3F

130. Due to Frenkel defect, the density of the ionic solids

- (1) Increases (2) Decreases
(3) Does not change (4) Changes

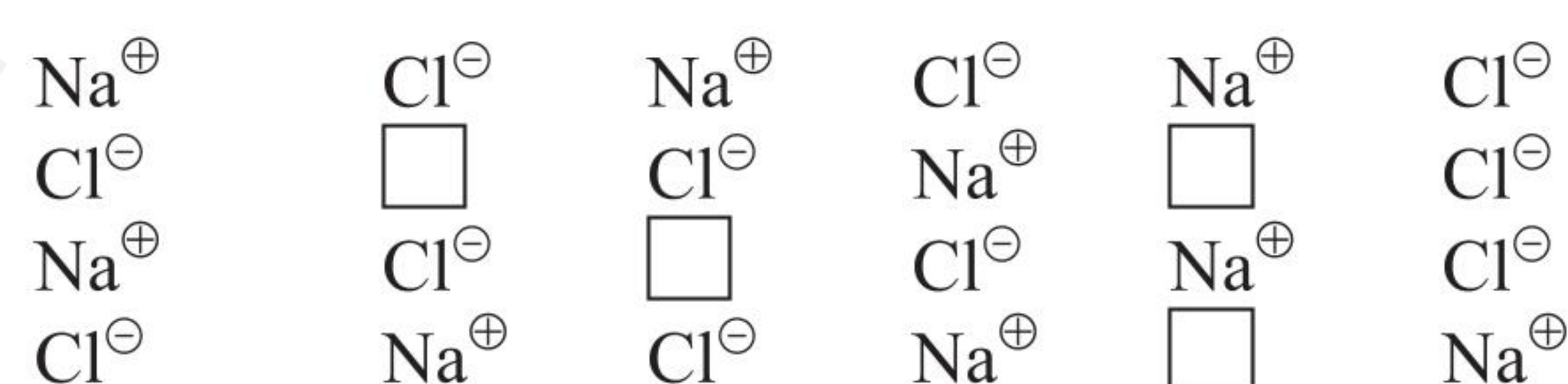
131. Which of the following is not a ferroelectric compound?

- (1) Rochelle salt (2) $\text{K}_4[\text{Fe}(\text{CN})_6]$
(3) BaTiO_3 (4) KH_2PO_4

132. The material used in solar cells contains

- (1) Cs (2) Si
(3) Sn (4) Ti

133. What type of crystal defect is indicated in the diagram given below



- (1) Both Frenkel and Schottky defects
(2) Schottky defect
(3) Interstitial defect
(4) Frenkel defect

134. Silicon doped with group 13 and group 15 member elements is, respectively, called semiconductor

- (1) *p*-type, *n*-type (2) *n*-type, *p*-type
(3) *p*-type (4) *n*-type

135. The electrical conductivity of semiconductor is

- (1) $10^8 \text{ ohm}^{-1} \text{ cm}^{-1}$
(2) $10^{-22} \text{ ohm}^{-1} \text{ cm}^{-1}$
(3) In the range of 10^{-9} to $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$
(4) None of the above

136. Pure silicon and germanium are

- (1) Conductors
(2) Insulators
(3) Semiconductors
(4) May be any one of the above

137. Which of the following is a ferroelectric compound?

- (1) BaTiO_3 (2) $\text{K}_4[\text{Fe}(\text{CN})_6]$
(3) Pb_2O_3 (4) None of these

138. Schottky defect to crystals is observed when

- (1) Unequal number of cations and anions are missing from the lattice.
- (2) Equal number of cations and anions are missing from the lattice.
- (3) An ion leaves its normal site and occupies an interstitial site.
- (4) Density of the crystal is increased.

139. Which of the following has Frenkel defect?

- (1) Sodium chloride
- (2) Graphite
- (3) Silver bromide
- (4) Diamond

140. To get *n*-type doped semiconductor, impurity to be added to silicon should have the following number of valence electrons

- (1) 2
- (2) 5
- (3) 3
- (4) 1

141. Superconductors are derived from the compounds of

- (1) *p*-block elements
- (2) Lanthanides
- (3) Actinides
- (4) Transition elements

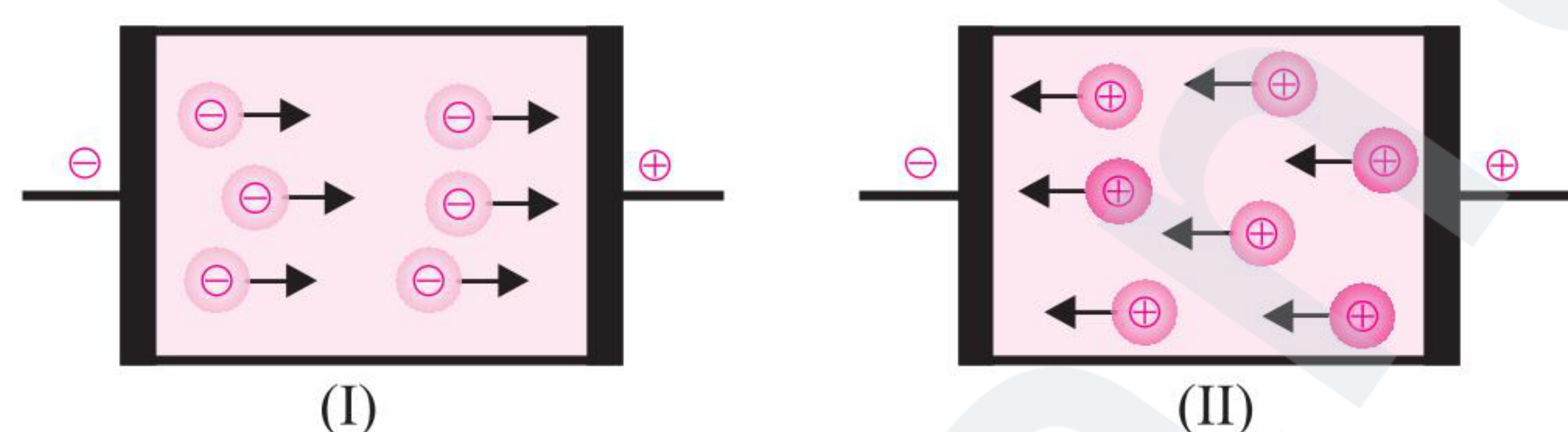
142. A semiconductor of Ge can be made *p*-type by adding

- (1) Trivalent impurity
- (2) Tetravalent impurity
- (3) Pentavalent impurity
- (4) Divalent impurity

143. Which of the following metal oxides is anti-ferromagnetic in nature?

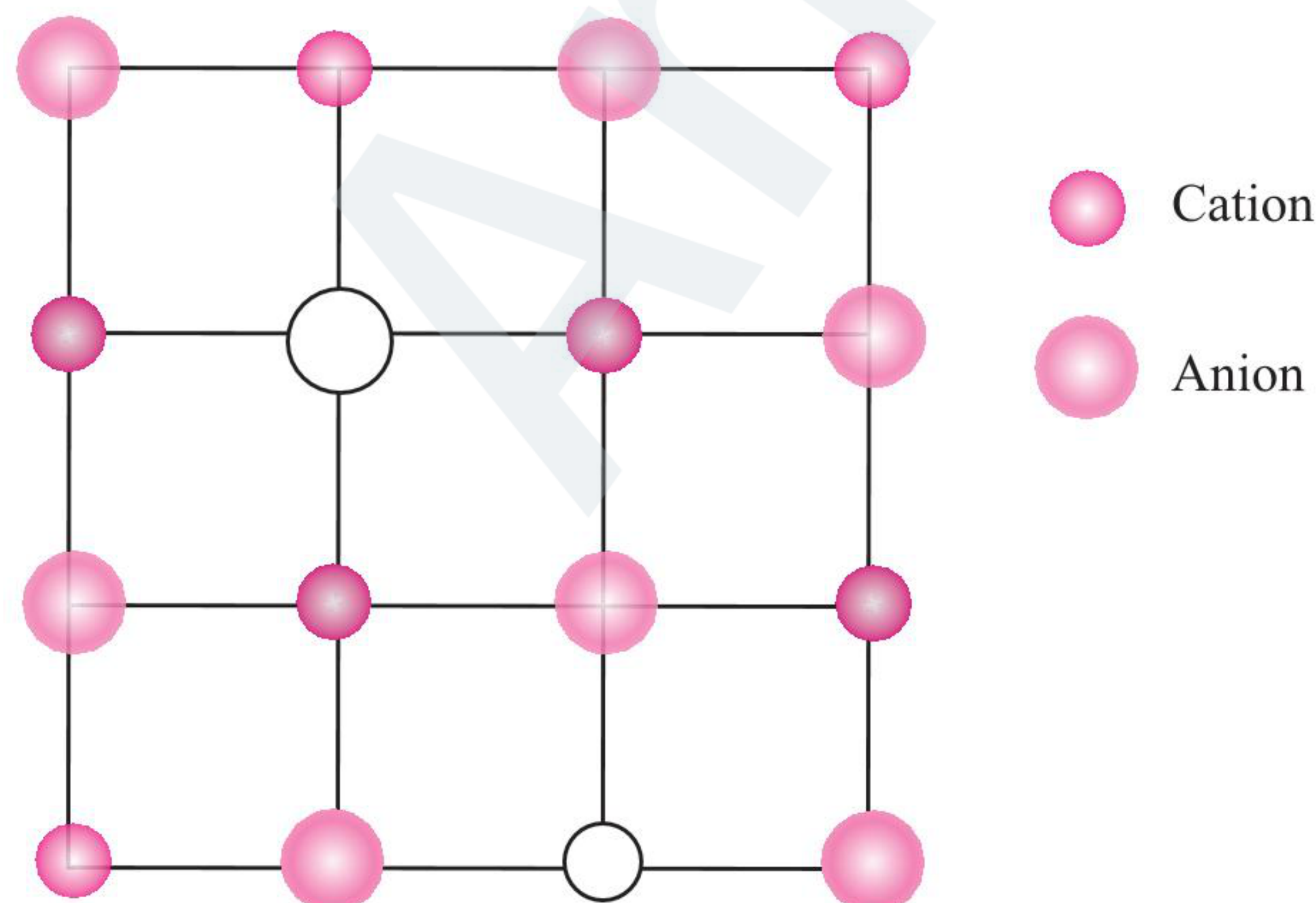
- (1) MnO_2
- (2) TiO_2
- (3) VO_2
- (4) CrO_2

144. What are types of following semiconductors I and II.



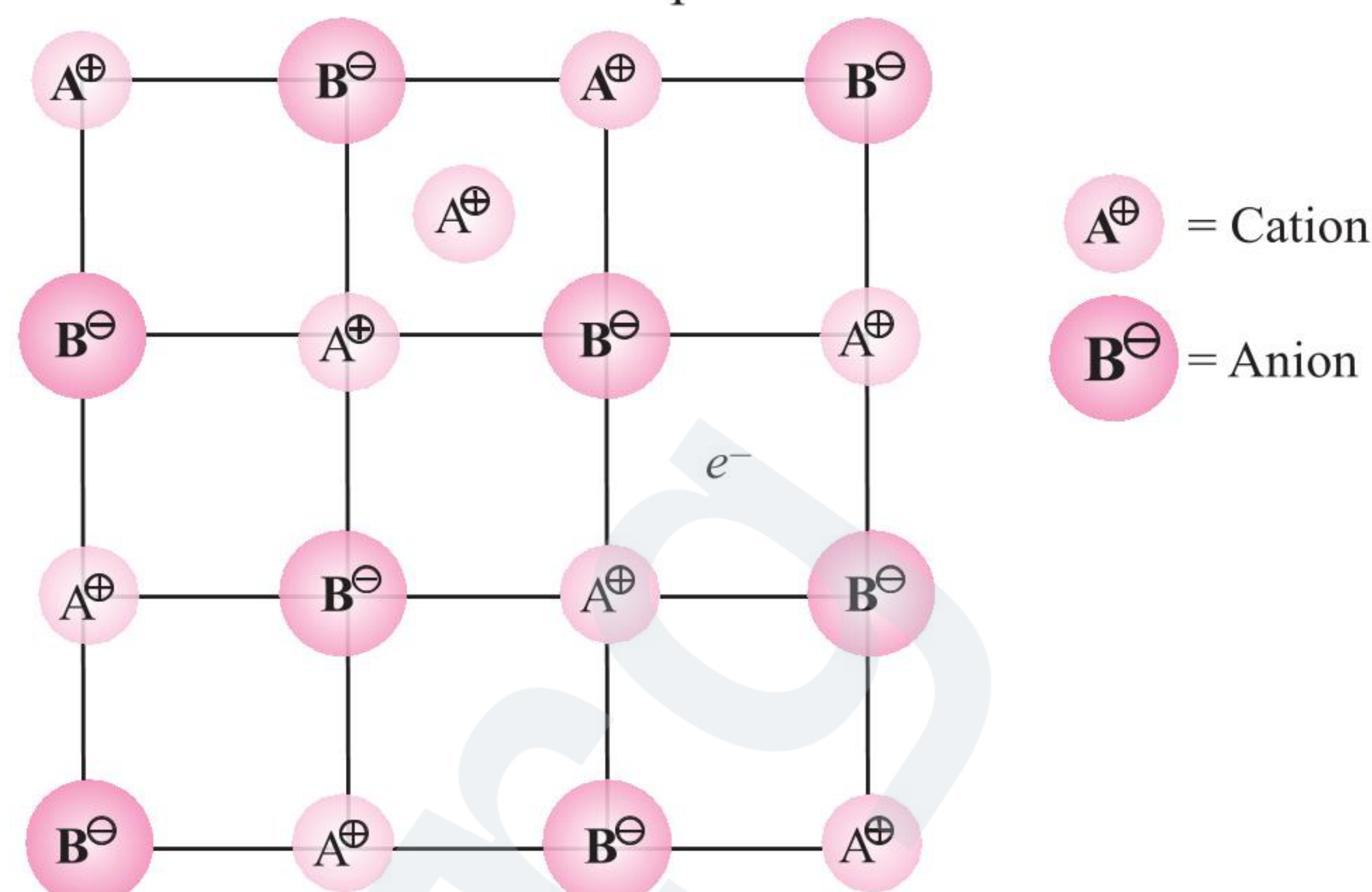
- (1) I $\Rightarrow$ *p*-type, II $\Rightarrow$ *n*-type
- (2) I $\Rightarrow$ *n*-type, II $\Rightarrow$ *p*-type
- (3) Both *n*-type
- (4) Both *p*-type

145. The structure shown here represents



- (1) Schottky defect
- (2) Frenkel defect
- (3) Metal excess defect
- (4) None

146. The structure shown here represents



- (1) Schottky defect
- (2) Frenkel defect
- (3) Metal excess defect because of absent anion
- (4) Metal excess defect because of excess cation

147. In AgCl , the Ag^+ ions are displaced from their lattice position to an interstitial position. Such a defect is called

- (1) Schottky defect
- (2) Frenkel defect
- (3) Wadsley defect
- (4) Colour centre

148. NaCl shows Schottky defects and AgCl shows Frenkel defects. Their electrical conductivity is due to the

- (1) Motion of electrons and not the motion of ions
- (2) Motion of ions and not the motion of electrons
- (3) Lower coordination number of NaCl
- (4) Higher coordination number of AgCl

149. Amorphous solids are classified as

- (1) Isotropic and supercooled liquids
- (2) Anisotropic and supercooled liquids
- (3) Isoenthalpic and supercooled liquids
- (4) Isotropic and superheated solids

150. Due of Frenkel defect

- (1) Density of the crystal decreases
- (2) Conduction increases
- (3) Conduction decreases
- (4) Crystal becomes charged electrically

151. Which of the following statements is/are correct?

- (1) All ferroelectric solids are piezoelectric.
- (2) All piezoelectric solids are ferroelectric.
- (3) Lead zirconate (PbZrO_3) is an antiferroelectric crystal.
- (4) BaTiO_3 (barium titanate) is a ferroelectric crystal.

152. Which of the following statements is/are correct?

- (1) A diode is a combination of *p*- and *n*-type semiconductors which is used as a rectifier.
- (2) Transistors are sandwich semiconductors of the type *pnp* or *nnp* which are used to detect or amplify radio or audio signals.
- (3) Monoxides of transition metals, all of which possess NaCl structures, show very large variations in electrical properties.
- (4) ReO_3 has the conductivity as well as appearance like that of copper.

153. Which of the following statements is/are correct?

- (1) Piezoelectric crystals are used as pick-ups in record players, they are also used in microphones, ultrasonic generators, and sonar detectors.
- (2) BaTiO_3 , Rochelle salt, KH_2PO_4 , and quartz are ferroelectric and piezoelectric solids.
- (3) The temperature above which no ferromagnetism is observed is called curie temperature.
- (4) The temperature at which the material shows superconductivity is called transition temperature.

Miscellaneous

154. Nearest distance between two tetrahedral voids and between two octahedral voids are respectively.

- (1) $\frac{a}{\sqrt{2}}, \frac{\sqrt{3}}{2}a$
- (2) $\frac{\sqrt{3}}{4}a, \frac{\sqrt{3}}{2}a$
- (3) $\frac{\sqrt{3}}{2}a, \frac{a}{\sqrt{2}}$
- (4) $\frac{\sqrt{3}}{2}a, \frac{\sqrt{3}}{4}a$

155. In sphalerite and antifluorite type structures, number of tetrahedral voids occupied are respectively.

- (1) 8, 4
- (2) 4, 8
- (3) 4, 0
- (4) 0, 4

156. Choose the correct option for hexagonal close packing of sphere in three dimensions

- (1) In one unit cell there are 12 octahedral voids and all are completely inside the unit cell.
- (2) In one unit cell there are six octahedral voids and all are completely inside the unit cell.
- (3) In one unit cell there are six octahedral voids and of which three are completely inside the unit cell and other three are from contributions of octahedral voids which are partially inside the unit cell.
- (4) In one unit cell there are 12 tetrahedral voids, all are completely inside the unit cell.

157. In a hexagonal closed packed system of crystals. assume, $C = 2 \times$ distance between two close packed layers, and (r) is the radius of every sphere.

The number of effective atoms and $\left(\frac{C}{r}\right)$ ratio in this hcp unit cell are respectively.

- (1) 8, $24\sqrt{2}r^3$
- (2) 6, $4 \times \sqrt{\frac{2}{3}}$
- (3) 12, $24\sqrt{2}r^3$
- (4) 12, $4 \times \sqrt{\frac{2}{3}}$

158. In rutile structure coordination number of cation and anion are respectively.

- (1) 6, 3
- (2) 3, 6
- (3) 6, 4
- (4) 4, 6

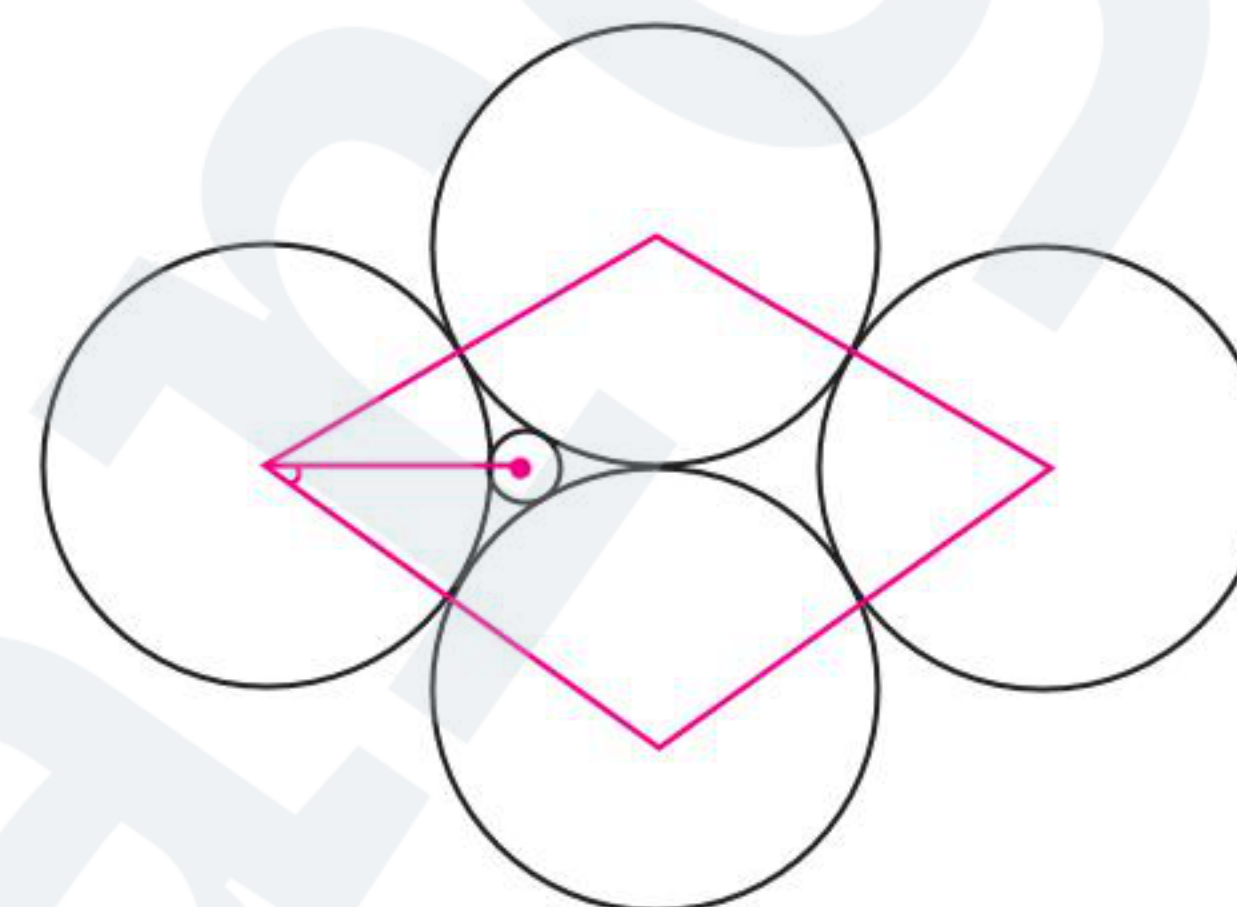
159. In spinel structure, ratio of tetrahedral to octahedral voids occupied and unoccupied are respectively:

- (1) 1:2 and 2:1
- (2) 7:2 and 1:2
- (3) 2:1 and 2:1
- (4) 2:7 and 2:1

160. If the radii of Mg^{2+} , Cs^+ , O^{2-} , S^{2-} and Cl^- ions are 0.65, 1.69, 1.40, 1.84, and 1.81 Å, respectively. The coordination number of the cations in the crystals of CsCl , MgS and MgO are respectively

- (1) 4, 8 and 6
- (2) 6, 4 and 8
- (3) 8, 4 and 6
- (4) 6, 6 and 8

161. Consider the parallelogram shown in the figure below representing two-dimensional unit cell. If R is the radius of larger circle and r is the radius of the triangular hole, the relation between r and R is:



- (1) $r = \left(\frac{2}{\sqrt{3}}\right)R$
- (2) $r = \left(\frac{\sqrt{2}}{3}\right)R$
- (3) $r = \left(\frac{2}{\sqrt{3}} - 1\right)R$
- (4) $r = \left(\frac{\sqrt{2}}{3} - 1\right)R$

162. There are five types of 2D- lattice which differ in the symmetry of arrangement of points. Which of the following 2D-lattice is not possible

- (1) Hexagonal
- (2) Pentagonal
- (3) Parallelogram
- (4) Rectangular

163. Metallic gold crystallises in the fcc lattice. The length of the cubic unit cell is $a = 4,242$ Å.

Closest distance between two gold atoms and packing factor are respectively.

- (1) $3.0 \text{ Å}, \frac{\sqrt{2}}{6} \pi$
- (2) $1.5 \text{ Å}, \frac{\sqrt{2}}{6} \pi$
- (3) $3.0 \text{ Å}, \frac{\sqrt{3}}{8} \pi$
- (4) $1.5 \text{ Å}, \frac{\sqrt{3}}{8} \pi$

164. Which of the following statements is INCORRECT for the diamond structure?

- (1) Each atom has 4 nearest neighbours and 12 next nearest neighbours.
- (2) It is relatively empty.
- (3) The maximum proportion of the available volume which may be filled by hard spheres is only 0.34.
- (4) The maximum proportion of the available volume which may be filled by hard spheres is only 0.46.

165. Which of the following statements is/are correct?

- I. Piezoelectric crystals are used as pick-ups in record players, they are also used in microphones, ultrasonic generators, and sonar detectors.
- II. BaTiO_3 , Rochelle salt, KH_2PO_4 , and quartz are ferroelectric and piezoelectric solids.
- III. The temperature above which no ferromagnetism is observed is called transition temperature.

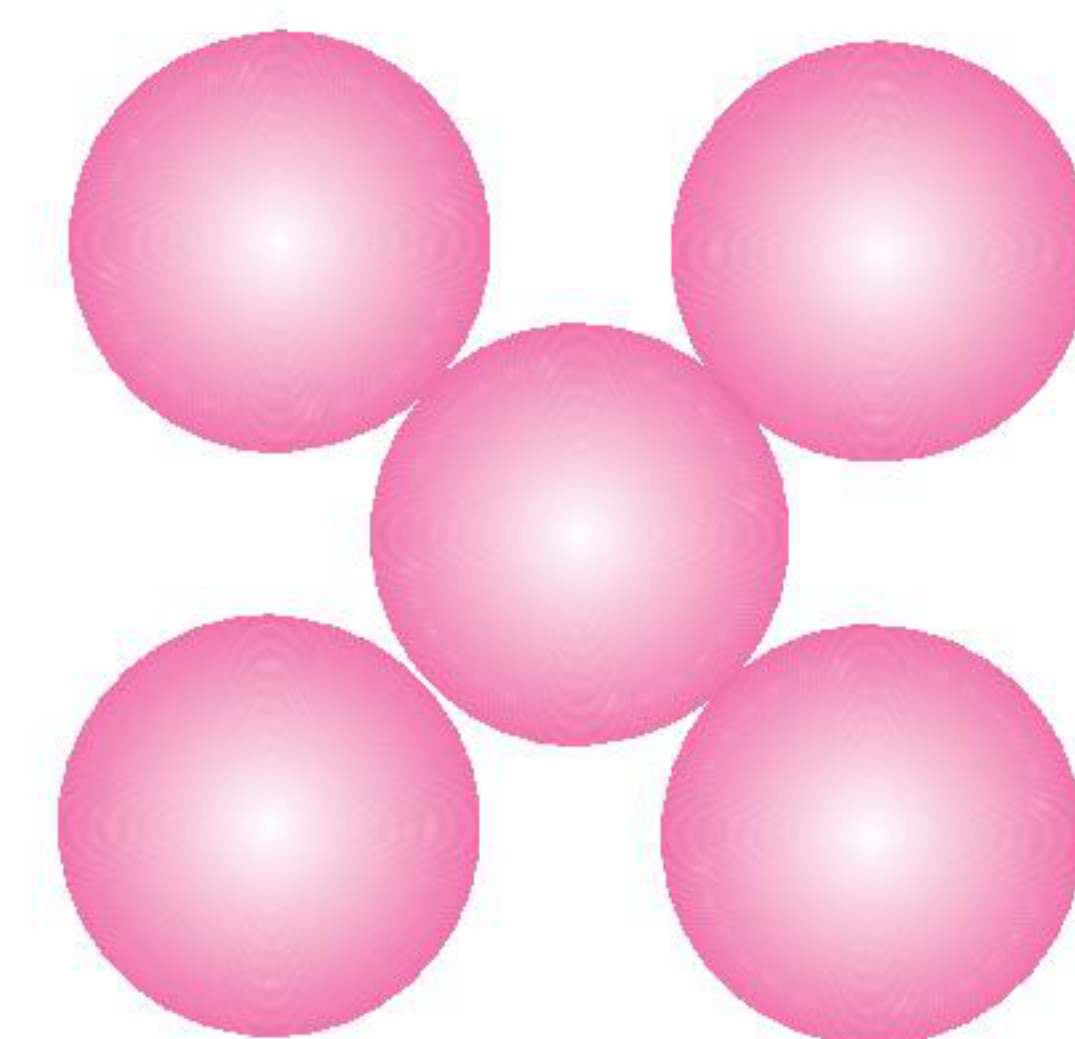
IV. The temperature at which the material shows superconductivity is called curie temperature.

- (1) I, II (2) II, III, IV
(3) I, II, III (4) All

Multiple Correct Answers Type

Classification of Solids and Their Properties

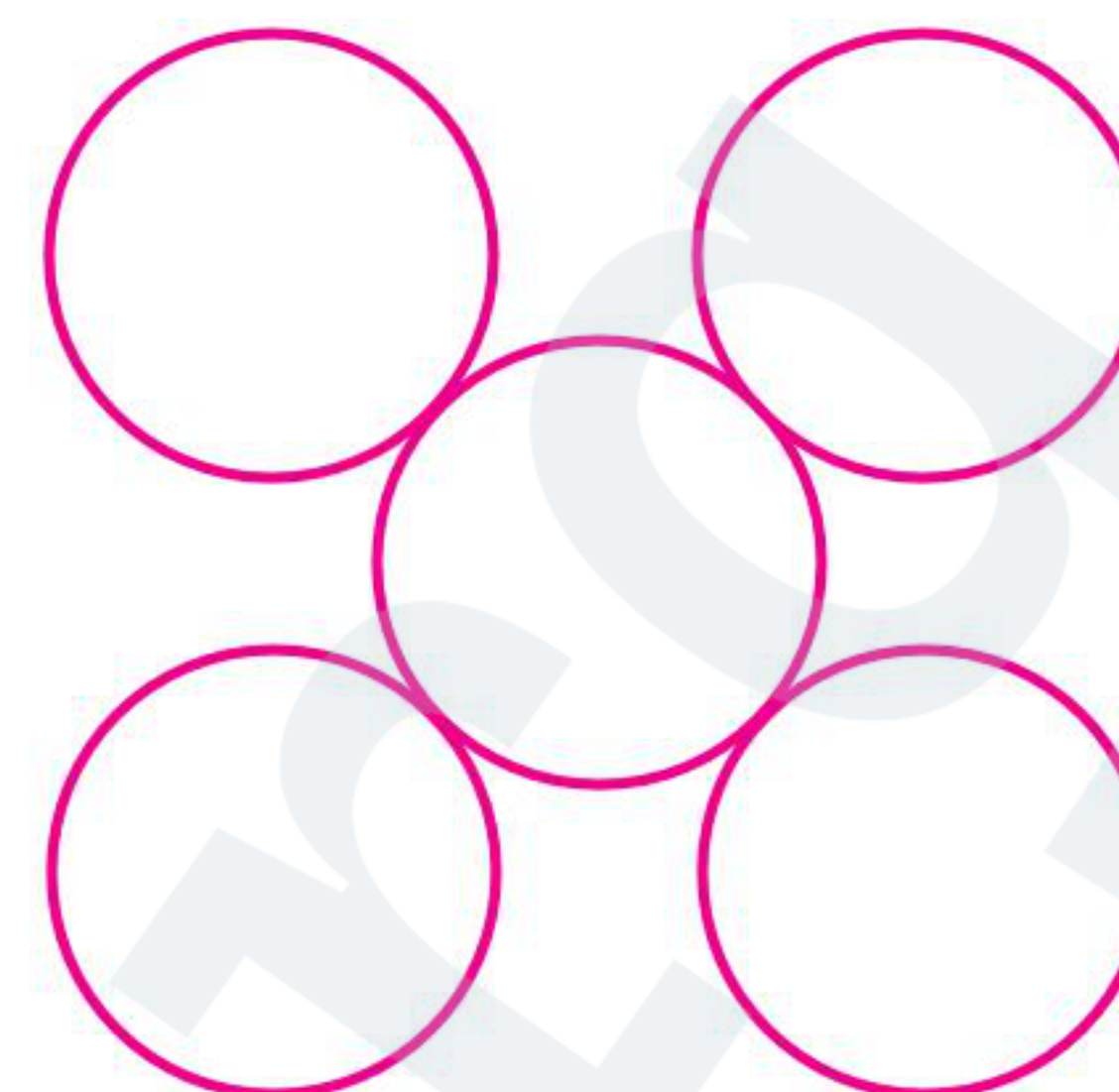
- An hcp and a ccp structure for a given element would be expected to have
 - The same coordination number
 - The same density
 - The same packing fraction
 - All of these
- Ions of NaCl which are touched by 1 body diagonal are
 - $\text{Cl}^\ominus$ ions present at the corner of cube
 - $\text{Cl}^\ominus$ ions present at the face centre of cube
 - $\text{Na}^\oplus$ ions present at the edge centre of cube
 - $\text{Na}^\oplus$ present at body centre of cube
- Which of the following statements is/are correct for both fluorite and antifluorite structures?
 - Cation is present in alternate TVs.
 - Anion constitutes lattice.
 - Number of formula unit in one unit cell is 4.
 - 100% tetrahedral voids are occupied.
- Identical spheres are undergoing two-dimensional packing in square close packing and hexagonal close packing. Which is correct regarding the spheres?
 - The ratio of coordination number for a sphere in first case to that in second case is 2 : 3.
 - Packing in second case is more effective.
 - Packing in first case is more effective.
 - The stacking of layer on first type packing produces simple cubic structure.
- For which of the following cases, answer is 4?
 - Coordination number of Zn^{2+} in Zinc blende
 - Number of body diagonal planes in a cube
 - Formula units in rock salt structure
 - Formula units in CsCl structure
- An octahedron has
 - 8 corners (2) 8 faces
 - 8 edges (4) 12 edges
- Aluminium metal has a density of 2.72 g cm^{-3} and crystallizes in a cubic lattice with an edge of 404 pm. Which is/are correct?
 - It forms an fcc unit cell.
 - It forms a bcc unit cell.
 - Its coordination number is 8.
 - Its coordination number is 12.
- If the radius of anion is 0.20 nm, the maximum radius of cations which can be filled in respective voids is correctly matched in
 - $r_\oplus = 0.0828 \text{ nm}$ for tetrahedral void
 - $r_\oplus = 0.045 \text{ nm}$ for triangular void
 - $r_\oplus = 0.1464 \text{ nm}$ for octahedral void
 - None of the above
- Select the correct statement(s) about three-dimensional hcp system.
 - The number of atoms in hcp unit cell is six.
 - The volume of hcp unit cell is $24\sqrt{2} r^3$.
 - The empty space in hcp unit cell is 26%.
 - The base area of hcp unit cell is $6\sqrt{3} r^2$.
- In which of the following systems primitives $a \neq b \neq c$?
 - Orthorhombic (2) Monoclinic
 - Triclinic (4) Hexagonal
- In which of the following systems interfacial angles $\alpha = \gamma = 90^\circ$ but $\beta \neq 90^\circ$?
 - Monoclinic (2) Rhombohedral
 - Triclinic (4) Hexagonal
- The space in which atoms are not present in unit cell is
 - In sc 48% (2) In fcc 26%
 - In bcc 32% (4) In hexagonal 26%
- Which of the following having their radius ratio between 0.414 and 0.732, i.e., for NaCl structure, have their radius ratio not in this range but possess NaCl-type structure?
 - LiBr (2) KCl
 - RbCl (4) BaO
- In the fluorite structure if the radius ratio is $\left(\sqrt{\frac{3}{2}} - 1\right)$, how many ions does each cation touch?
 - 4 anions (2) 12 cations
 - 8 anions (4) No cations
- If the radius of $\text{Cs}^\oplus = 1.69 \text{ \AA}$ and $\text{Br}^\ominus = 1.95 \text{ \AA}$, then which of the following is/are correct statement?
 - The edge length of unit cell is 4.2 \AA.
 - The coordination number for $\text{Cs}^\oplus$ is 6.
 - CsBr has bcc-type structure.
 - $\text{Br}^\ominus$ ions touch each other along the edge.
- Given is the arrangement of atoms in a crystallographic plane. Which plane correctly represent(s) the adjacent drawn structure?
 - Face plane in fcc
 - Body diagonal plane in fcc
 - Face plane in bcc
 - Body diagonal plane in bcc



17. Graphite is
 (1) A good conductor (2) sp^2 hybridized
 (3) An amorphous solid (4) A covalent crystal
18. Diamond is
 (1) A covalent solid (2) A non-conductor
 (3) A lubricant (4) sp^3 hybridized
19. The density of KBr is 2.75 g cm^{-3} . The length of the unit cell is 654 pm. Atomic mass of K = 39, Br = 80. Then what is true about the predicted nature of the solid?
 (1) The unit cell is fcc.
 (2) $Z = 4$.
 (3) There are four constituents/unit cells.
 (4) There are 8 ions at corners and 6 at the centres of the faces.
20. What is true about a bcc unit cell?
 (1) The number of atoms in the unit cell is 2.
 (2) In addition to an atom at the centre of the body, in a unit cell there are 8 atoms at 8 different corners.
 (3) One-eighth of an atom at a corner of the unit cell.
 (4) None of the above.
21. What is true about simple cubic type of unit cells?
 (1) Eight constituents are at different corners of the cube.
 (2) $Z_{\text{eff}} = 1$.
 (3) Contribution by one corner is 1/8th of an atom.
 (4) None of the above.
22. Which of the following is/are covalent solids?
 (1) Fe (2) Diamond (3) NaCl (4) Graphite
23. Which is/are not amorphous solid(s)?
 (1) Rubber (2) Graphite (3) Glass (4) Plastics
24. Which is/are correct statement ?
 (1) Packing fraction in 2D-hcp is 0.785
 (2) Packing fraction in AAA..... is 0.52
 (3) Packing fraction in ABAB..... is 0.74
 (4) Void fraction in ABCABC..... is 0.26
25. Given : Radius of $A^{2+} = 100 \text{ pm}$; Radius of $C^{\oplus} = 240 \text{ pm}$; Radius of $B^{2-} = 300 \text{ pm}$; Radius of $D^{\ominus} = 480 \text{ pm}$ Which is/are correct statement ?
 (1) Coordination number of A^{2+} in compound AB is 4
 (2) Coordination number of A^{2+} in compound AB is 6
 (3) Coordination number of $C^{\oplus}$ in compound CD is 6
 (4) Coordination number of $C^{\oplus}$ in compound CD is 8
26. If the three interaxial angles defining the unit cell are all equal in magnitude, the crystal cannot belong to the
 (1) Orthorhombic system (2) Cubic system
 (3) Hexagonal system (4) Triclinic system
27. Crystal systems in which no two axial lengths are equal are:
 (1) Tetragonal (2) Orthorhombic
 (3) Monoclinic (4) Triclinic

28. Given is the arrangement of atoms in crystallographic plane. Which plane correctly represent(s) the drawn structure?

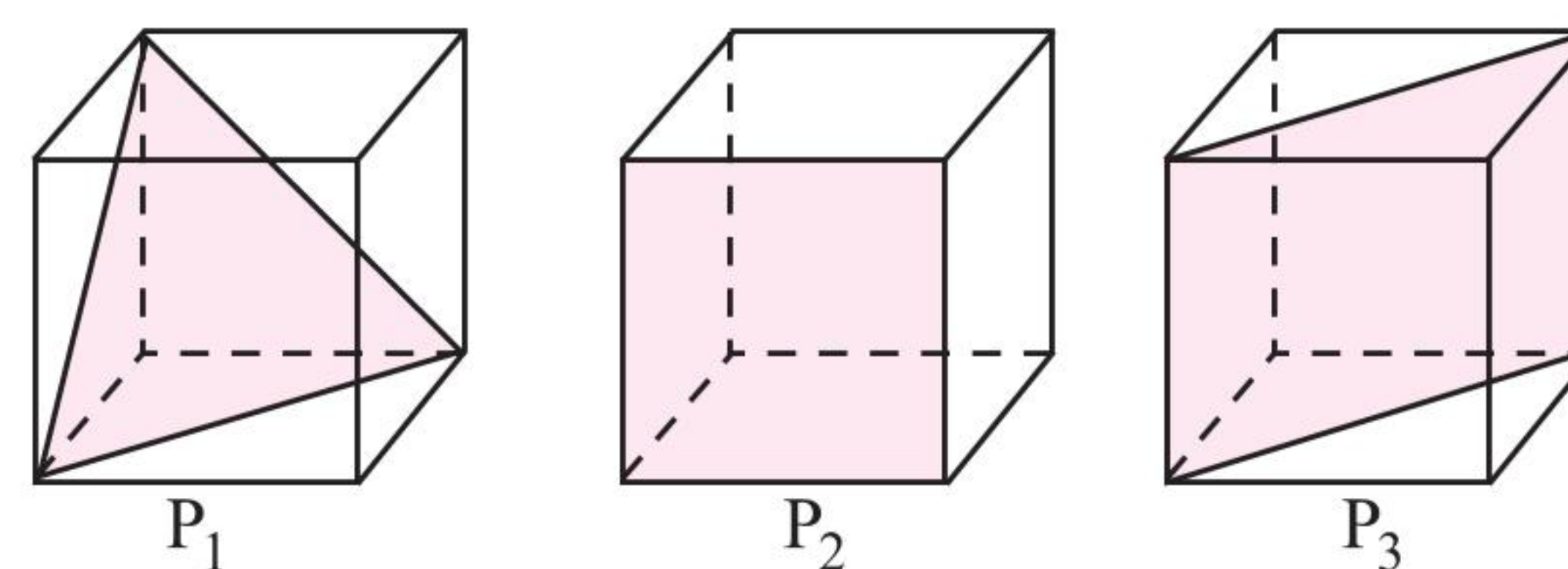
- (1) Face plane in fcc (2) Body diagonal plane in fcc
 (3) Face plane in bcc (4) Body diagonal plane in bcc



29. Potassium crystallizes in body-centred cubic lattice. Then
 (1) The distance between nearest neighbors is $4.50 \text{ \AA}$
 (2) The distance between next-nearest neighbors is $5.20 \text{ \AA}$
 (3) Each K have nearest neighbors equal to 4.
 (4) Each K have nearest neighbors equal to 6.

Tetrahedral and Octahedral Voids

30. Position of OVs in an fcc structure is
 (1) Corners of unit cell
 (2) Edge centre of unit cell
 (3) Body centre of unit cell
 (4) Face centre of unit cell
31. For the spinel structure (MgAl_2O_4), the correct statement is/are
 (1) 50% OVs are occupied by ions.
 (2) Al^{3+} is equally distributed in TVs and OVs.
 (3) Oxide ions occupy ccp lattice.
 (4) 12.5% TVs are occupied by ions.
32. Following three planes (P_1 , P_2 , P_3) in an fcc unit cell are shown in the figure below. Consider the following statements and choose the correct option/options that follow:



- (1) P_1 contains no three-dimensional voids.
 (2) P_2 contains only octahedral voids.
 (3) P_3 contains both octahedral and tetrahedral voids.
 (4) All of these
33. Position of octahedral voids in fcc structure is/are
 (1) Edge centre of unit cell
 (2) Body centre of unit cell
 (3) Corners of unit cell
 (4) Face centre of unit cell

- 34.** Position of TVs in closest packed structure is/are
- (1) Edge centre of unit cell
 - (2) Two TVs on each body diagonal
 - (3) Position of each TV from corner is $\sqrt{3}a/4$.
 - (4) Face centre of unit cell
- 35.** Which of the following statements is/are correct about TVs in an fcc unit cell?
- (1) Number of TVs per atom in fcc unit cell is 2.
 - (2) Number of TVs per unit cell is 8.
 - (3) Number of TVs is twice the number of atoms in the fcc unit cell.
 - (4) Number of TVs is equal to the number of atoms in the fcc unit cell.
- 36.** Which of the following statements is/are correct about TVs in an fcc unit cell?
- Given: Edge length = a
Body diagonal = b
- (1) Each TV lies at a distance $b/4$ from the nearest corner.
 - (2) Each TV lies at a distance $3b/4$ from the farthest corner.
 - (3) Each TV lies at a distance of $\sqrt{3}a/4$ from the nearest corner.
 - (4) The distance between two TVs is $b/2$.
- 37.** If the radius of Na^+ is 95 pm and that of Cl^- ions is 181 pm then:
- (1) Co-ordination no. of Na^+ is 6
 - (2) Co-ordination no. of Cl^- is 8
 - (3) Length of the unit cell is 552 pm
 - (4) Length of the unit cell is 380 pm
- 38.** Select the correct statement(s):
- (1) A NaCl type AB crystal lattice can be interpreted to be of two individual fcc type unit lattice of A^+ and B^- fused together in such a manner that the corner of one unit lattice becomes the edge centre of the other
 - (2) In a fcc unit cell, the body centre is an octahedral void
 - (3) In an sc lattice, there can be no octahedral void
 - (4) In an sc lattice, the body centre is the octahedral void
- 39.** Which of the following is not true about the voids formed in 3 dimensional hexagonal close packed structure?
- (1) A tetrahedral void is formed when a sphere of the second layer is present above triangular void in the first layer
 - (2) All the triangular voids are not covered by the spheres of the second layer
 - (3) Tetrahedral voids are formed when the triangular voids in the second layer lie above the triangular voids in the first layer and the triangular shapes of these voids do not overlap
 - (4) Octahedral voids are formed when the triangular voids in the second layer exactly overlap with similar voids in the first layer
- 40.** The co-ordination number of fcc structure for metals is 12, since
- (1) Each atom touches 4 others in same layer, 3 in layer above and 3 in layer below
 - (2) Each atom touches 4 others in same layer, 4 in layer above and 4 in layer below
 - (3) Each atom touches 6 others in same layer, 3 in layer above and 3 in layer below
 - (4) Each atom touches 3 others in same layer, 6 in layer above and 6 in layer below
- 41.** In the unit cell of NaCl, which of the following statements are correct?
- (1) Na^+ ions have six Cl^- ions in its nearest neighbourhood
 - (2) Cl^- ion have six Na^+ ion in its nearest neighbourhood
 - (3) Second nearest neighbour of Na^+ ion are twelve Na^+ ions
 - (4) NaCl has 68% of occupied space.
- 42.** Sodium oxide Na_2O is a crystalline solid. It has:
- (1) Antifluorite structure
 - (2) Na^+ ions are present at body diagonals
 - (3) Na^+ ions are present at tetrahedral voids
 - (4) O^{2-} ions are present at octahedral voids
- 43.** Select the correct statements among the following :
- (1) Nearest neighbour distance in NaCl = $\frac{a}{2}$
 - (2) Nearest neighbour distance in CaF_2 = $\frac{a\sqrt{3}}{4}$
 - (3) Nearest neighbour distance in Na_2O = $\frac{a\sqrt{3}}{4}$
 - (4) Nearest neighbour distance in CsCl = $\frac{a\sqrt{3}}{2}$
- Defects in crystals**
- 44.** Which of the following statements is/are correct?
- (1) Dislocation of ion from lattice site to interstitial site is called Frenkel defect.
 - (2) Missing of +ve and -ve ions from their respective position producing a pair of holes is called Schottky defect.
 - (3) The presence of ions in the vacant interstitial sites along with lattice point is called interstitial defect.
 - (4) Non-stoichiometric NaCl is yellow solid.
- 45.** Select the correct statement(s).
- (1) The conductance through electrons is called p -type conduction.

- (2) The conductance through positive holes is called *p*-type conduction.
- (3) The conductance through electrons is called *n*-type conduction.
- (4) The band gap in germanium is small.
- 46.** Select the correct statement(s).
- (1) Solids with F-centres are paramagnetic.
- (2) Ferrimagnetic character of Fe_3O_4 at room temperature changes to paramagnetic character at 850 K.
- (3) Anti-ferrimagnetic V_2O_3 changes to paramagnetic at 150 K.
- (4) Non-stoichiometric Cu_2O is a *p*-type semiconductor.
- 47.** Non-stoichiometric compounds are
- (1) Cu_2O (2) Cu_2S
- (3) FeO (4) $\text{Hg}_2\text{Ba}_2\text{YCaCu}_2\text{O}_7$
- 48.** Recently discovered superconductivity materials are
- (1) M_3C_{60} (2) $\text{YBa}_2\text{Cu}_3\text{O}_7$
- (3) SiC (4) $\text{Hg}_2\text{Ba}_2\text{YCaCu}_2\text{O}_7$
- 49.** If a mixture of LiCl and NaCl is melted and then cooled,
- (1) A solid solution is formed.
- (2) Mixture formed is called eutectic mixture.
- (3) $\text{TiO}_{1.8}$ is non-stoichiometric solid solution of Ti_2O_3 and TiO_2 .
- (4) Neither LiCl nor NaCl separates.
- 50.** Which of the following statements is/are correct?
- (1) If three Fe^{2+} ions are missing from their lattice in FeO , then there must be two Fe^{3+} ions somewhere in the lattice.
- (2) Crystals with metal deficiency defects are called superconductors.
- (3) Crystals with metal deficiency are called semiconductors.
- (4) 1 Bohr Magneton = $9.27 \times 10^{-24} \text{ A m}^2$
- 51.** Select the correct statement(s).
- (1) The non-stoichiometric form of NaCl is yellow and that of KCl is blue-lilac.
- (2) Solids containing F-centres (Farbe) are paramagnetic.
- (3) Non-stoichiometric compounds are called Berthollide compounds.
- (4) Conduction by electrons is called *n*-type semiconductors.
- 52.** A mineral having the formula AB_2 crystallizes in the ccp lattice, with A atoms occupying the lattice points. Select the correct statement(s).
- (1) The coordination number (CN) for A atoms = 8.
- (2) The CN for B atom = 4.
- (3) 100% of TVs are occupied by B atoms
- (4) 50% of TVs are occupied by B atoms.
- 53.** An excess of potassium ions makes KCl crystals appear violet or lilac in colour since.....
- (1) Some of the anionic sites are occupied by an unpaired electron
- (2) Some of the anionic sites are occupied by a pair of electrons
- (3) There are vacancies at some anionic sites
- (4) F-centres are created which impart colour to the crystals
- 54.** The correct statement(s) regarding defects in solids is (are):
- (1) Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion
- (2) Frenkel defect is a dislocation defect
- (3) Trapping of an electron in the lattice leads to the formation of F-centre
- (4) Schottky defects have no effect on the physical properties of solids.
- 55.** The correct statement(s) for alkali halides is/are:
- (1) Metal excess defects make NaCl yellow.
- (2) Metal excess defects make LiCl , NaCl and KCl coloured.
- (3) Metal excess defects make NaCl yellow but has no effect on LiCl
- (4) Metal excess defects make both NaCl and KCl coloured.
- 56.** Which of the following is/are correct about the point defects?
- (1) In frenkel defect, the dielectric constant of solid increases
- (2) In Schottky defect, the density of solid decreases
- (3) In Frenkel defect, the density of solid decreases
- (4) In Schottky defect, the dielectric constant of solid increases
- 57.** Which of the following statements are correct?
- (1) Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic.
- (2) Ferrimagnetic substances do not lose ferrimagnetism on heating and remain ferrimagnetic.
- (3) Antiferromagnetic substances have domain structures similar to ferromagnetic substances and their magnetic moments are not cancelled by each other.
- (4) In ferromagnetic substances, all the domains get oriented in the direction of magnetic field and remain as such even after removing the magnetic field.
- 58.** Superconductors are technologically and commercially important substances. The correct information(s) about such conductors are:
- (1) Phenomena of superconductivity was first discovered by Kammerlingh and Onnes
- (2) Mercury acts as superconductor at 4 K
- (3) Superconductors offer zero resistance at zero kelvin
- (4) Gallium acts as superconductor at 4 K

Linked Comprehension Type

Paragraph 1

The “OLIVINE” series of minerals consists of crystals in which Fe^{2+} and Mg^{2+} ions may substitute for each other causing substitutional impurity defects without changing the volume of unit cell. In “OLIVINE” series of minerals, O^{2-} ions exist as fcc with Si^{4+} occupying one-fourth of OV's and divalent metal ions occupying one-fourth of TV's. The density of “forsterite” (magnesium silicate) is 3.21 g cm^{-3} and that of “fayalite” (ferrous silicate) is 4.34 g cm^{-3} .

1. The formula of “fayalite mineral” is:

- (1) Fe_2SiO_4 (2) FeSiO_4
(3) Fe_2SiO_6 (4) FeSiO_3

2. If in “forsterite mineral” bivalent Mg^{2+} ions are to be replaced by unipositive Na^+ ions, and if Na^+ ions are occupying half of TV's in fcc lattice, the arrangement of rest of the constituents is kept same, then the formula of the new solid is:

- (1) Na_2SiO_4 (2) Na_2SiO_3
(3) Na_4SiO_4 (4) $\text{Na}_2\text{Si}_2\text{O}_6$

3. The percentage of “fayalite” in an “OLIVINE” with density 3.88 g cm^{-3} approximately is:

- (1) 75% (2) 59%
(3) 35% (4) 29%

Paragraph 2

AX, AY, BX, and BY have rock salt type structure with following internuclear distances:

Salt	Anion–anion distance in Å	Cation–anion distance in Å
AX	2.40	1.70
AY	1.63	1.15
BX	2.66	1.88
BY	2.09	1.48

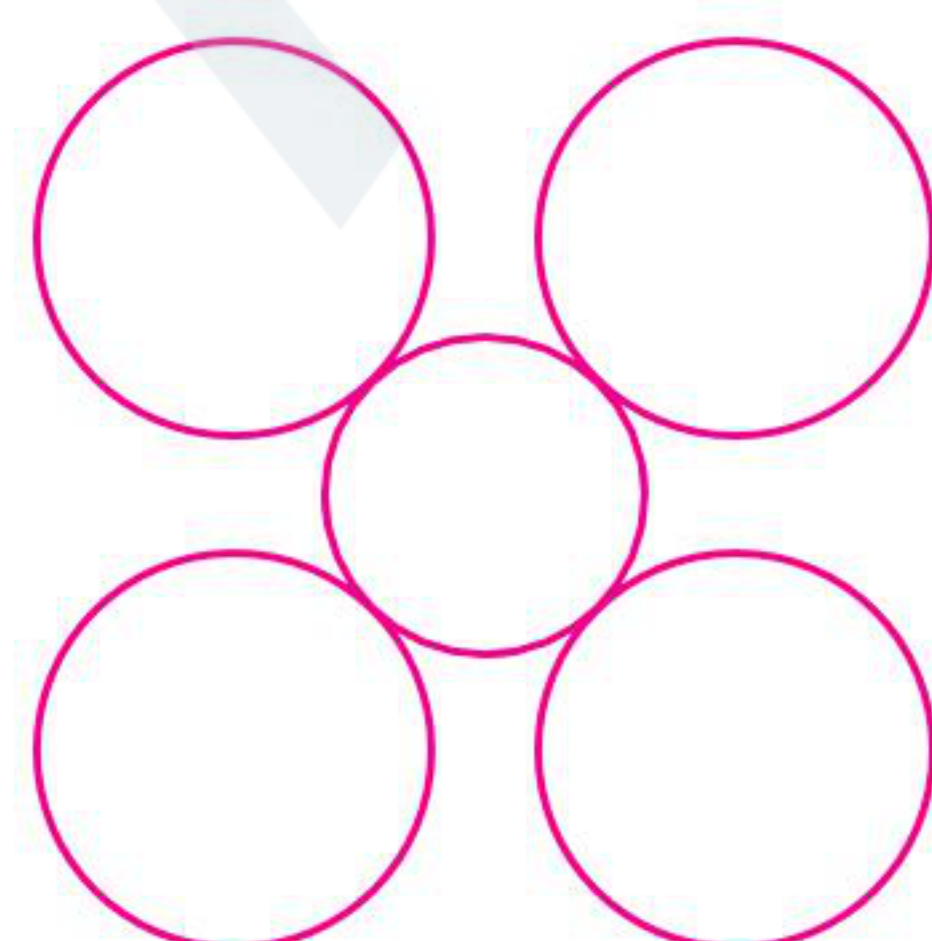
4. Ionic radii of A^+ and B^+ , respectively, are

- (1) 0.35 and 0.68 Å (2) 0.68 and 0.35 Å
(3) 1.20 and 0.80 Å (4) 0.80 and 1.20 Å

5. Ionic radii of X^- and Y^- , respectively, are

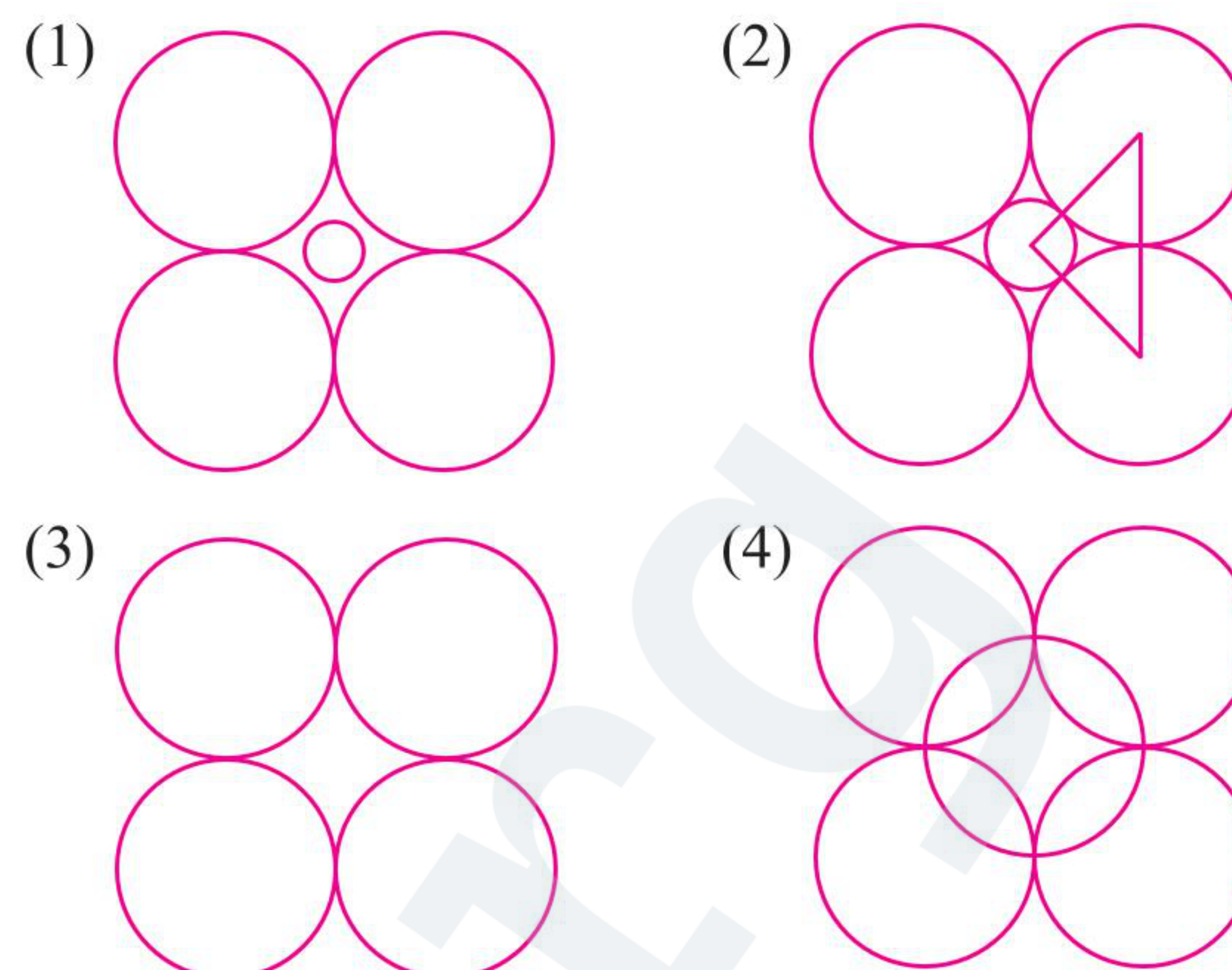
- (1) 0.35 and 0.68 Å (2) 0.68 and 0.35 Å
(3) 1.20 and 0.80 Å (4) 0.80 and 1.20 Å

6. The structure given below is of



- (1) AX (2) AY, BX
(3) AY, BX, BY (4) AY, BX, BY, and KCl

7. Which of the following structure is, respectively, by AX?

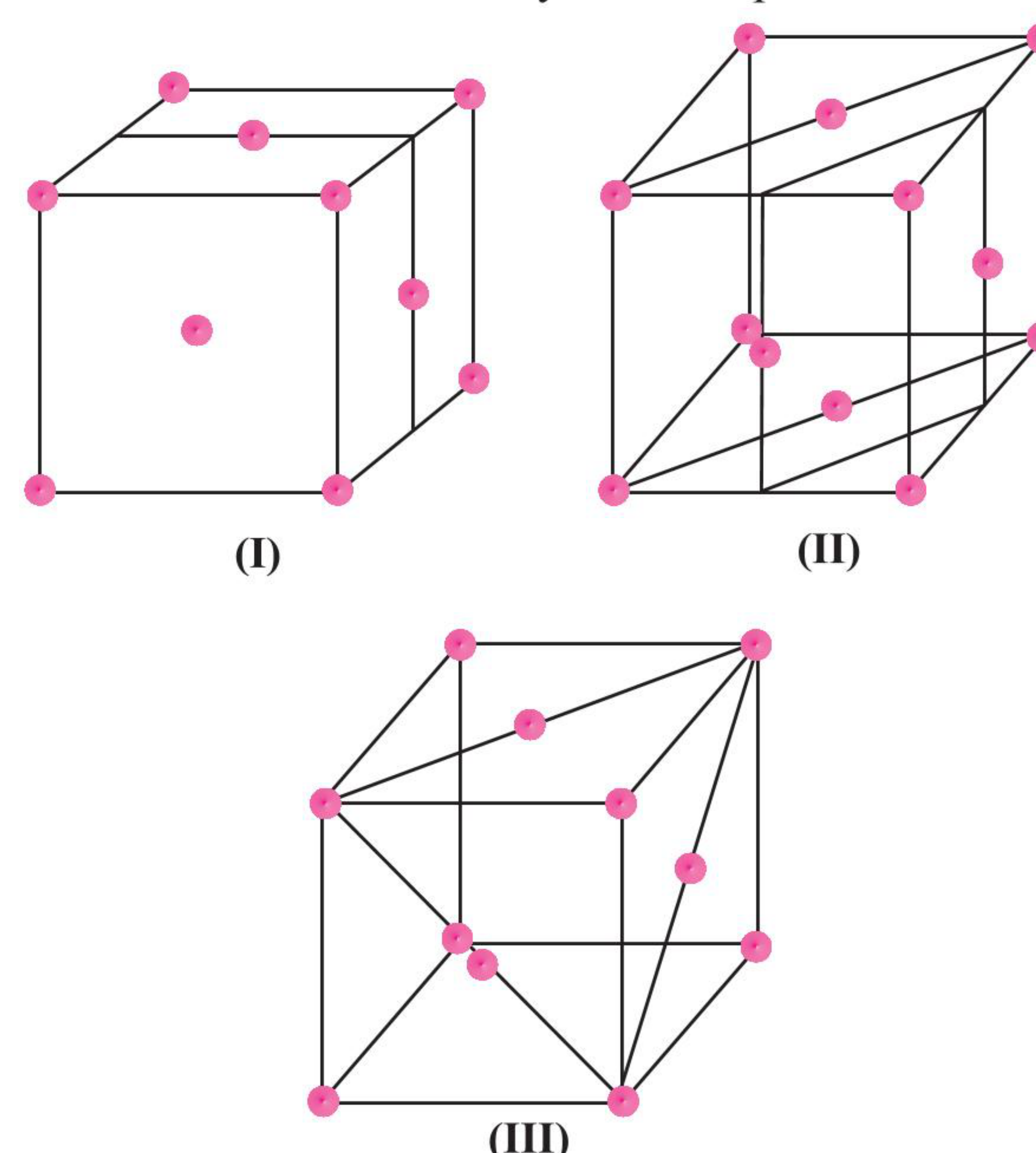


8. A salt MY crystallizes in the CsCl structure. The anions at the corners touch each other and cation is in the centre. The radius ratio (r_+/r_-) for this structure is

- (1) 0.225 (2) 0.414
(3) 0.732 (4) 1.0

Paragraph 3

The length of a unit cell (a) in the Ni crystal is 0.352 nm. The diffraction of X-rays of 0.154 nm wavelength (λ) from a Ni crystal occurs at 22.2° , 25.9° , and 38.2° . By using Bragg's law, ($n\lambda = 2d \sin \theta$), and assuming that the diffractions are first order ($n = 1$), the distances are calculated to be 0.204 nm, 0.176 nm and 0.124 nm. The various structures for the Ni crystal are represented as:



9. The distance (d) of 0.204 nm represent which structure?

- (1) I (2) II
(3) III (4) All

10. The distance (d) of 0.176 nm represent which structure?

- (1) I (2) II
(3) III (4) None

11. The distance (d) of 0.124 nm represent which structure?

- (1) I (2) II
(3) III (4) All

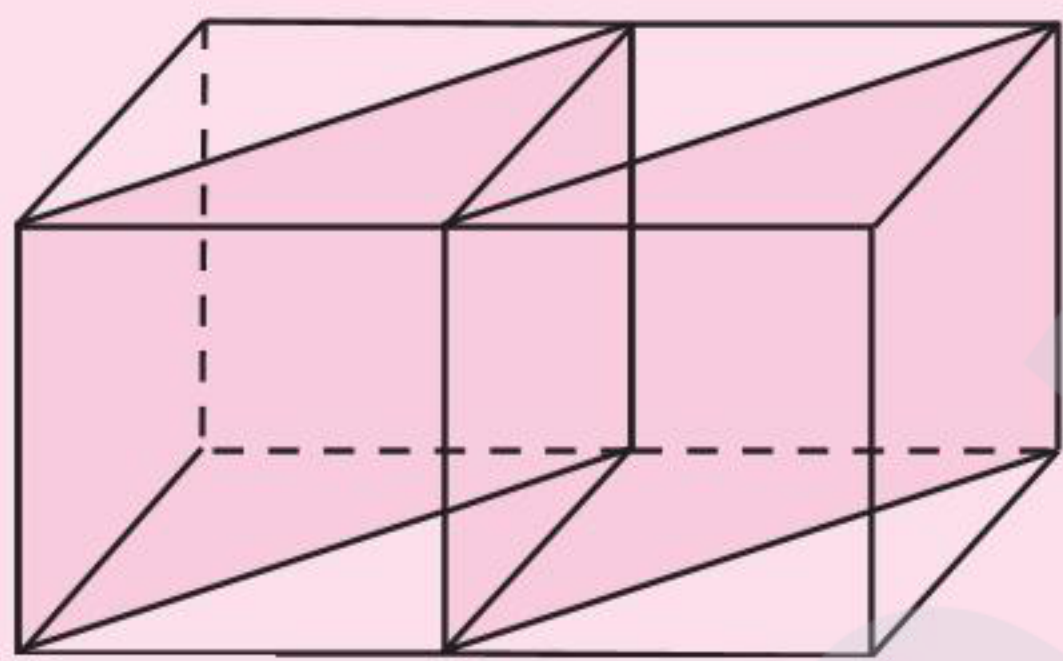
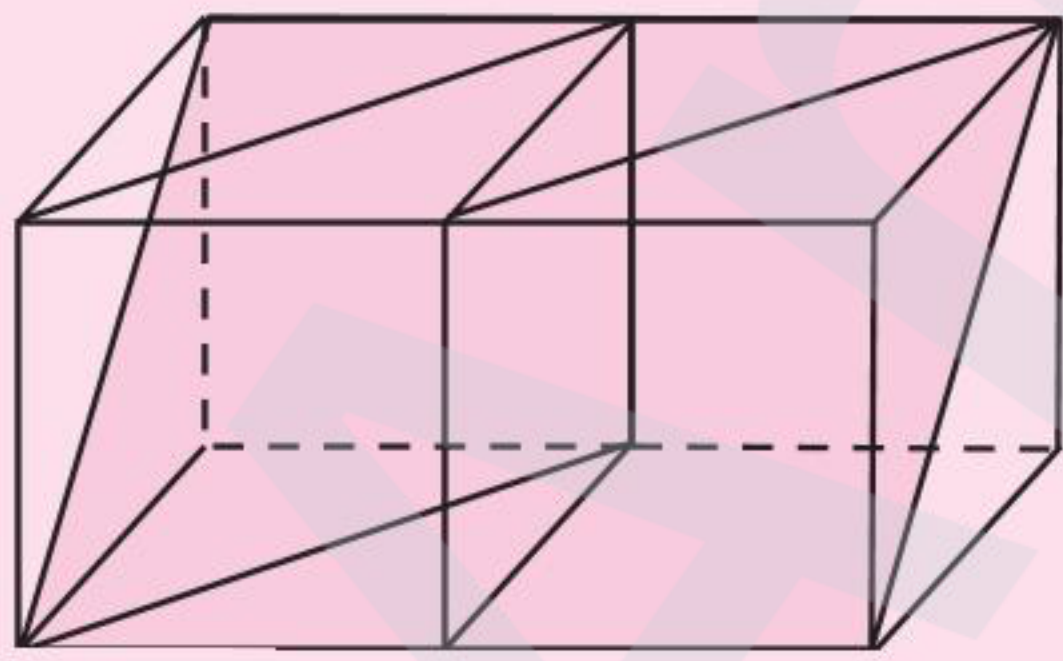
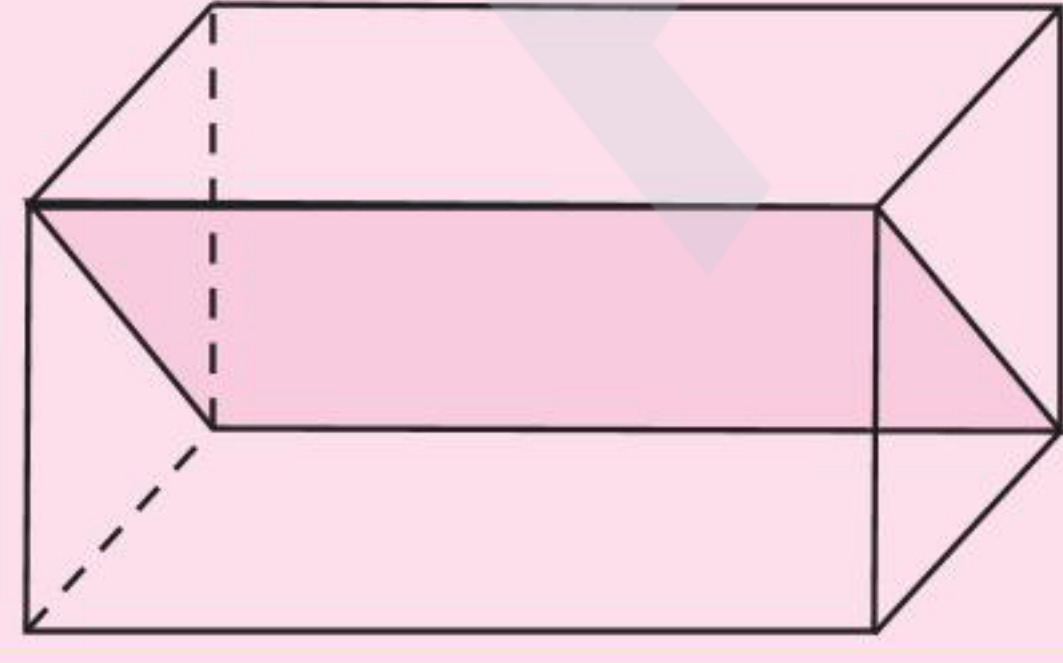
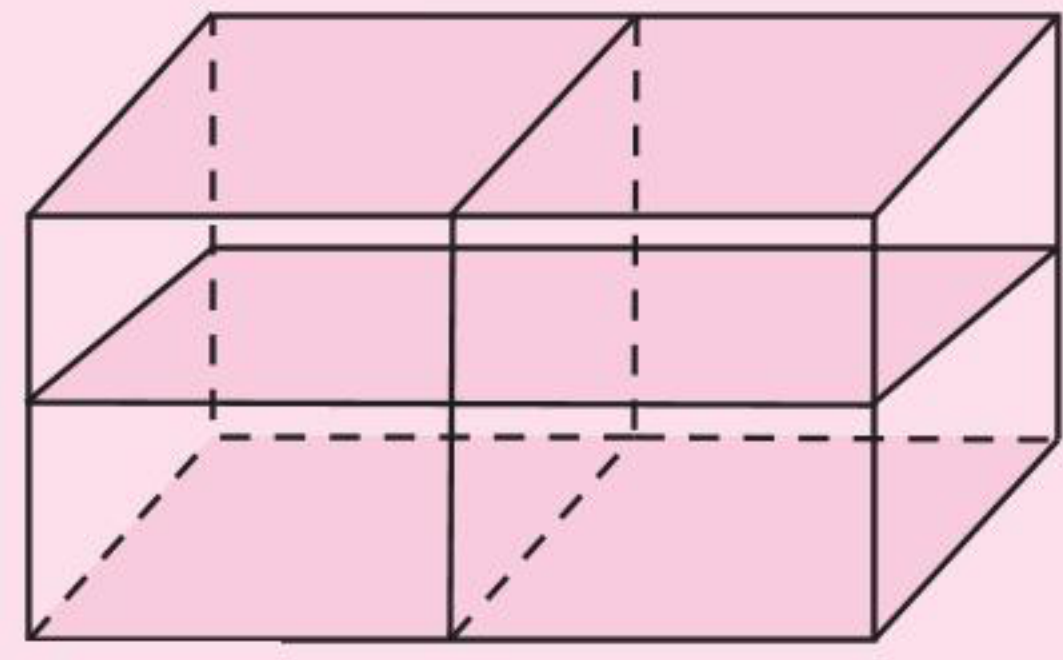
12. Which of the following statements is correct?
- (1) I represents sc-type structure
 - (2) II represents bcc-type structure
 - (3) III represents both sc- and bcc-type structure.
 - (4) All figures represent fcc-type structure.

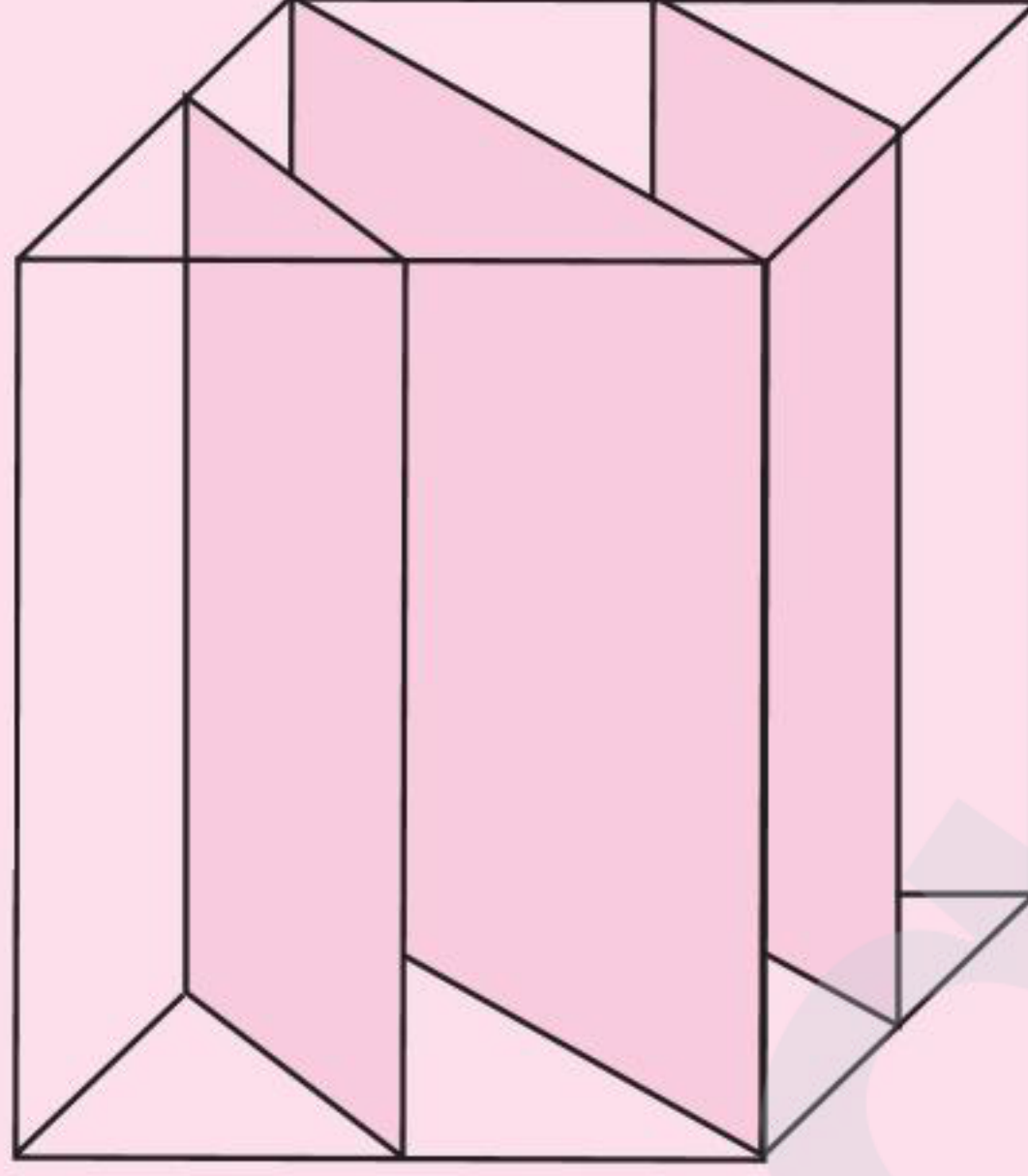
Matrix Match Type

This section contains questions each with two columns—I and II. Match the items given in column I with that in column II.

1.	Column I	Column II
	Elements of symmetry (For a cube)	Ions touched (In NaCl structure)
a.	Body diagonal	p. Only 2 face centre ions
b.	C ₄ axis (tetrad axis)	q. Only 2 corners ions
c.	Rectangular plane	r. Body centre ion
		s. Only one octahedral void

2.	Column I	Column II
a.	F-centres	p. Extra cations present in interstitial sites
b.	Metal excess defect	q. Some cations are replaced by one of higher valence
c.	Metal deficiency defect	r. Both cations and anions are missing from lattices
d.	Schottky defects	s. Electrons trapped in anionic vacancies

3.	Column I	Column II
	Type of crystal structure	Type of plane
a.		p. 101
b.		q. 110
c.		r. 022
d.		s. 101

e.		t.	220
----	---	----	-----

4.	Column I	Column II
	Compounds	Name of structure
a.	Fe ^{III} (Fe ^{II} Fe ^{III})O ₄	p. Rutile structure
b.	Mg ^{II} Al ₂ ^{III} O ₄ and Co ^{II} (Co ^{III}) ₂ O ₄	q. Inverse 2 : 3 spinel structure
c.	MnO ₂ and SnO ₂	r. Normal 2 : 3 spinel structure
d.	BaTiO ₃	s. Perovskite structure
e.	CaF ₂ and SrCl ₂	t. Fluorite-type structure

5.	Column I	Column II
a.	Even value of $h + k + l$	p. AgBr
b.	Substances having both Schottky and Frenkel defects	q. Insulator
c.	Devices that convert electrical energy to mechanical strain and vice versa	r. bcc structure
d.	Materials having conductivity range $10^{-10} - 10^{-20} \text{ S m}^{-1}$	s. Piezoelectric crystal
e.	Substances having a rutile structure	t. NaCl
f.	Substance having Schottky defects	u. Coordination number 6 : 3

6.	Column I	Column II
	Types of crystal	Location of cations/anions
a.	Na ₂ O	p. Anions = fcc Cations = Alternate TVs
b.	CaF ₂	q. Anions = fcc Cations = All TVs
c.	ZnS	r. Cations = fcc Anions = All TVs
d.	NaCl	s. Anions = fcc Cation = $\frac{1}{8}$ TVs + $\frac{1}{2}$ OVs
e.	Spinel (MgAl ₂ O ₄)	t. Anions = hcp Cations = 2/3 of OVs
f.	Corundum	u. Anions = fcc Cations = All OVs

For Q.7 to Q10: Answer the question given below by appropriately matching the information given in three column of the following table

Column I		Column II		Column III	
Statement		Characteristics (I)		Characteristics (II)	
a	In the FCC unit cell, two voids are formed on each non parallel body diagonal of the cube	i	All octahedral voids are empty	p	Coordination number = 4:4
b	In the FCC unit cell voids are formed at the body centre of the cube and on edge centre	ii	4 void / unit cell	q	Nearest distance between two atoms = $\frac{\sqrt{3} a}{4}$
c	FCC structure with 4 more atoms that are present in the alternate tetrahedral voids	iii	8 void / unit cell	r	Nearest distance between two voids = $\frac{a}{\sqrt{2}}$
d	CCP arrangement in which A^{2-} ion form FCC and each B^{2+} ion is surrounded tetrahedrally by A^{2-} ions and vice versa. B^{2+} ions are in alternate tetrahedral voids	iv	Packing efficiency = 34%	s	Nearest distance between two voids = $\frac{1}{2}$ × Body diagonal
				t	Nearest distance between two voids = $\frac{\sqrt{3} a}{2}$

7. Which of the following combination correctly represents the Tetrahedral voids?
(1) a—iii—s, t (2) a—iii—s
(3) b—iii—i (4) b—ii—p
8. Which of the following combination correctly represents the Octahedral voids?
(1) a—iii—s (2) b—ii—s
(3) c—iv—q (4) b—ii—r
9. Which of the following combination correctly represents the structure of “diamond cubic”?
(1) a—iii—t (2) c—iv—q
(3) c—iv—r (4) d—i—p
10. Which of the following combination represents crystal structure of Sphalerite type?
(1) a—i—p (2) b—ii—r
(3) d—i—p (4) d—i—r

at all faces of cubical crystal is 6×10^{30} , then the area of one face of cubical crystal is $A \times 10^{16} \text{ m}^2$. Find the value of A.

3. O^{2-} ions are arranged in ccp in a spinel structure. A^{2+} ions occupy 1/8 of TVs and $B^{\oplus}$ ions occupy half of OV. The void volume of unit cell = 0.11 A. Find the value of A.
4. Find the coordination number of $Na^{\oplus}$ in Na_2O .
5. A bcc lattice is made up of hollow spheres of B. Spheres of solids A are present in hollow spheres of B. The radius of A is half of the radius of B. The ratio of total volume of spheres of B unoccupied by A in a unit cell and volume of unit cell is $A \times \frac{\pi\sqrt{3}}{64}$. Find the value of A.
6. Give the total score of the correct statements of the following.

Statements		Score
a.	In an antiferroite structure, cations are present in all TVs.	1
b.	If the radius of cation is 0.35 pm and that of anion is 0.95 pm, then the CN of the crystal is 4.	2
c.	An atom or ion is transferred from a lattice site to an interstitial position in Frenkel defect.	3
d.	The density of a crystal always decreases in point defects.	4

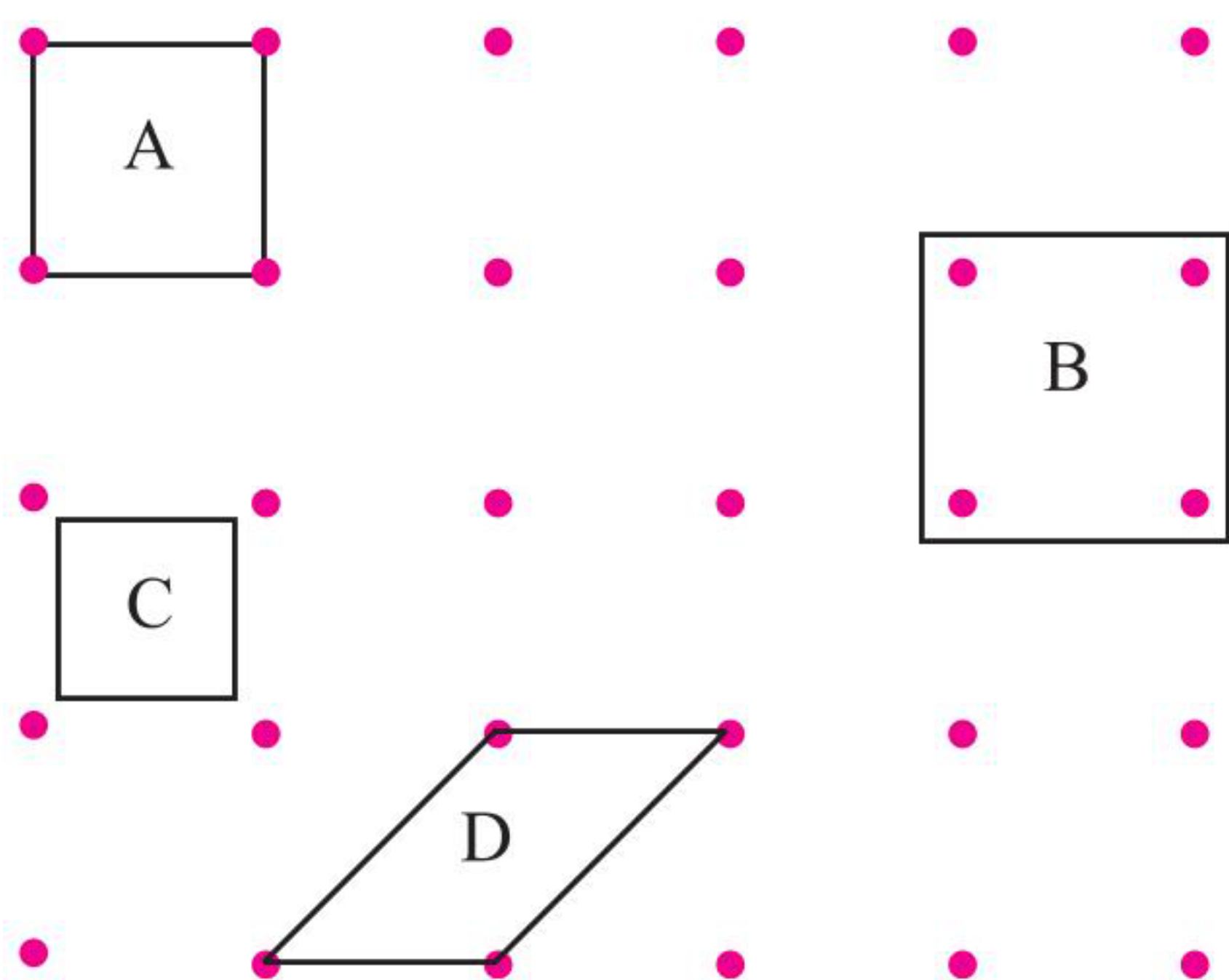
Numerical Value Type

1. If a solid $A^{\oplus}B^{\ominus}$ having ZnS structure is heated so that the ions along two of the axis passing through the face centre particles are lost and bivalent ion (Z) enters here to maintain the electrical neutrality, so that the new formula unit becomes $A_xB_yZ_c$, report the value of $x + y + c$.
2. Metal M of radius 50 nm is crystallized in fcc type and made cubical crystal such that face of unit cells aligned with face of cubical crystal. If the total number of metal atoms of M

7. Give the total score of the correct statements of the following.

Statements	Score
a. First two nearest neighbour distances for sc lattice are, respectively, a and $\sqrt{2}a$.	4
b. First two nearest neighbour distances for bcc lattice are, respectively, $\frac{\sqrt{3}a}{2}$ and a .	3
c. In ZnS (wurtzite), Zn^{2+} ions occupy lattice point while in ZnS (zinc blende), Zn^{2+} ions occupy alternate TVs.	2
d. In point defects, volume and geometry of the crystal do not change.	1

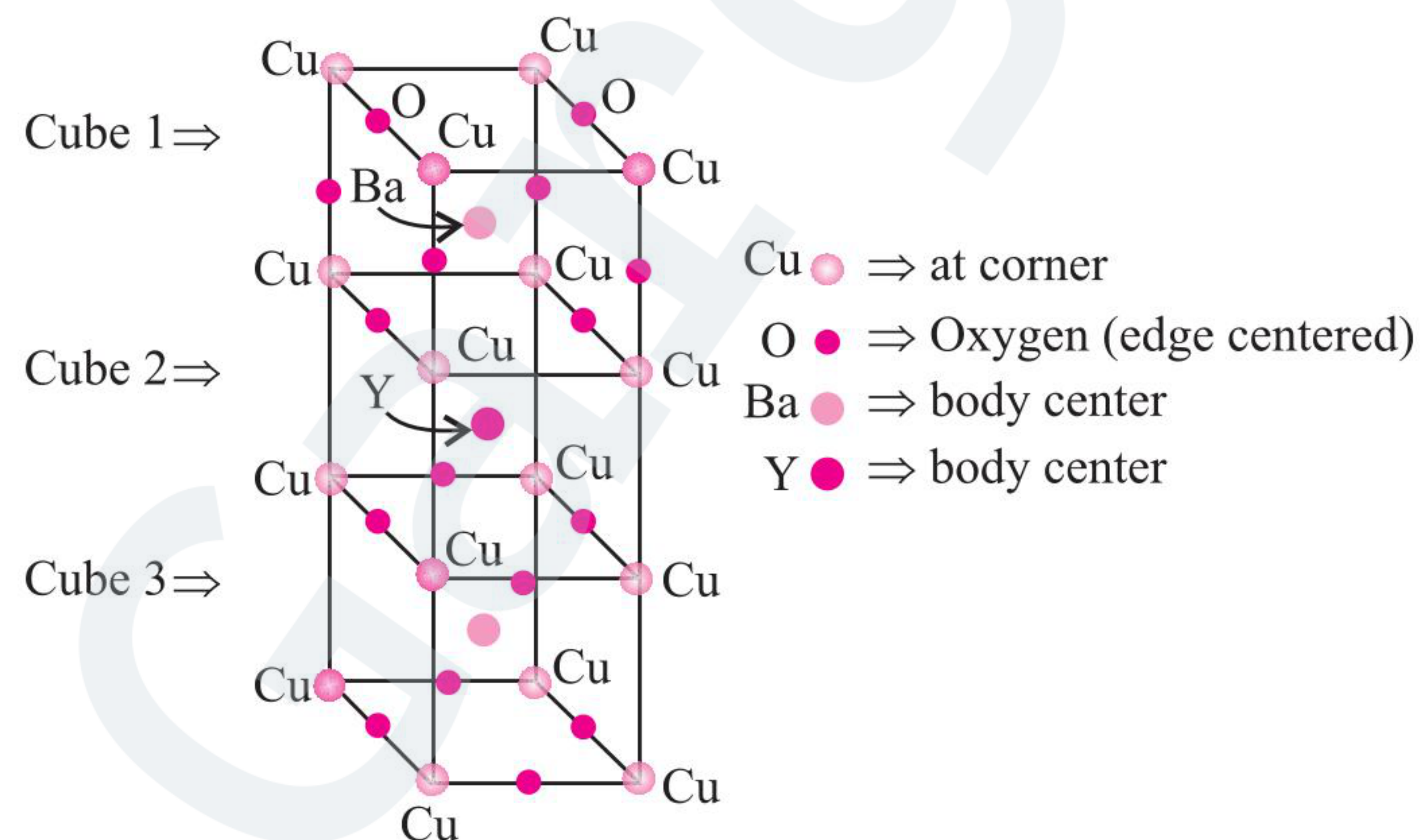
8. In the figure given below, four parallelograms are shown. How many parallelograms are unit cells?



9. Caesium atoms are the largest naturally occurring atoms. The radius of Cs atom is $2.6 \text{ \AA}$. The number of moles of Cs atoms to be laid side by side to give a row of Cs atoms 2.50 cm long is $x \times 10^{-17}$. Find the value of x .

Note: For Q.10, the integer value is between 10 and 20.

10. The following figure shows the unit cell of a compound, i.e., a mixed oxide of yttrium, barium, and copper. The formula of mixed oxide is $\text{Y}_a\text{Ba}_b\text{Cu}_c\text{O}_d$. Find the value of $(a + b + c + d)$.



11. A solid has a structure in which X atoms are located at cubic corners of unit cell, O atoms are at the edge centres and Y atoms at cube centre.

Then the formula of compound is $\text{X}_a\text{Y}_b\text{O}_c$.

If two atoms of O are missing from any of two edge centres per unit cell, then the molecular formula is $\text{X}_x\text{Y}_y\text{O}_z$.

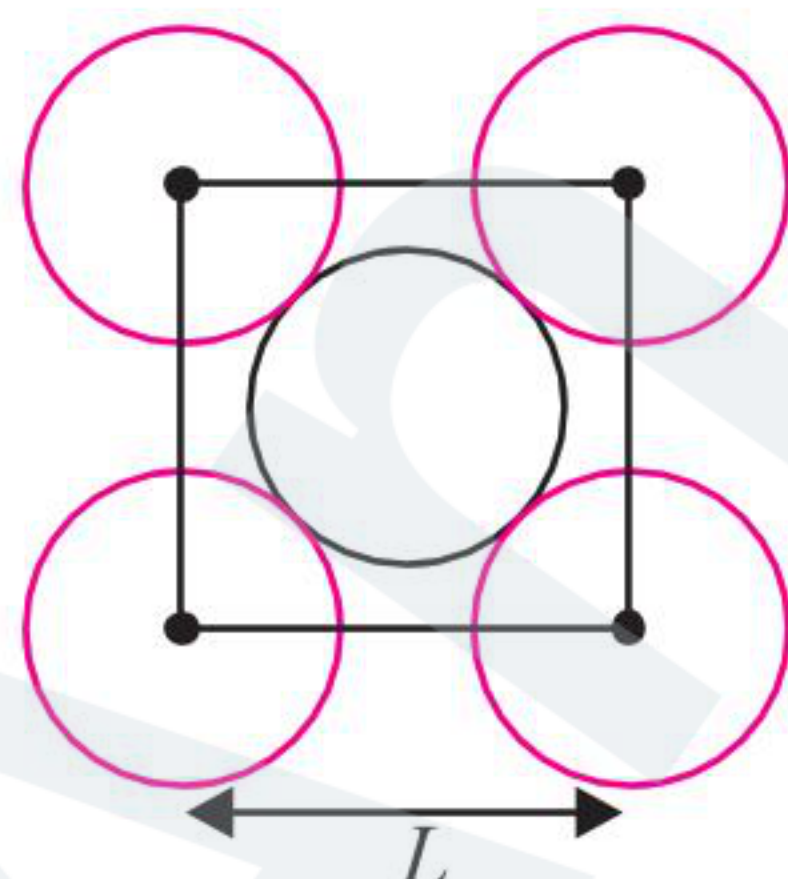
Then, find the value of $(x + y + z) - (a + b + c)$.

Archives

JEE ADVANCED

Single Correct Answer Type

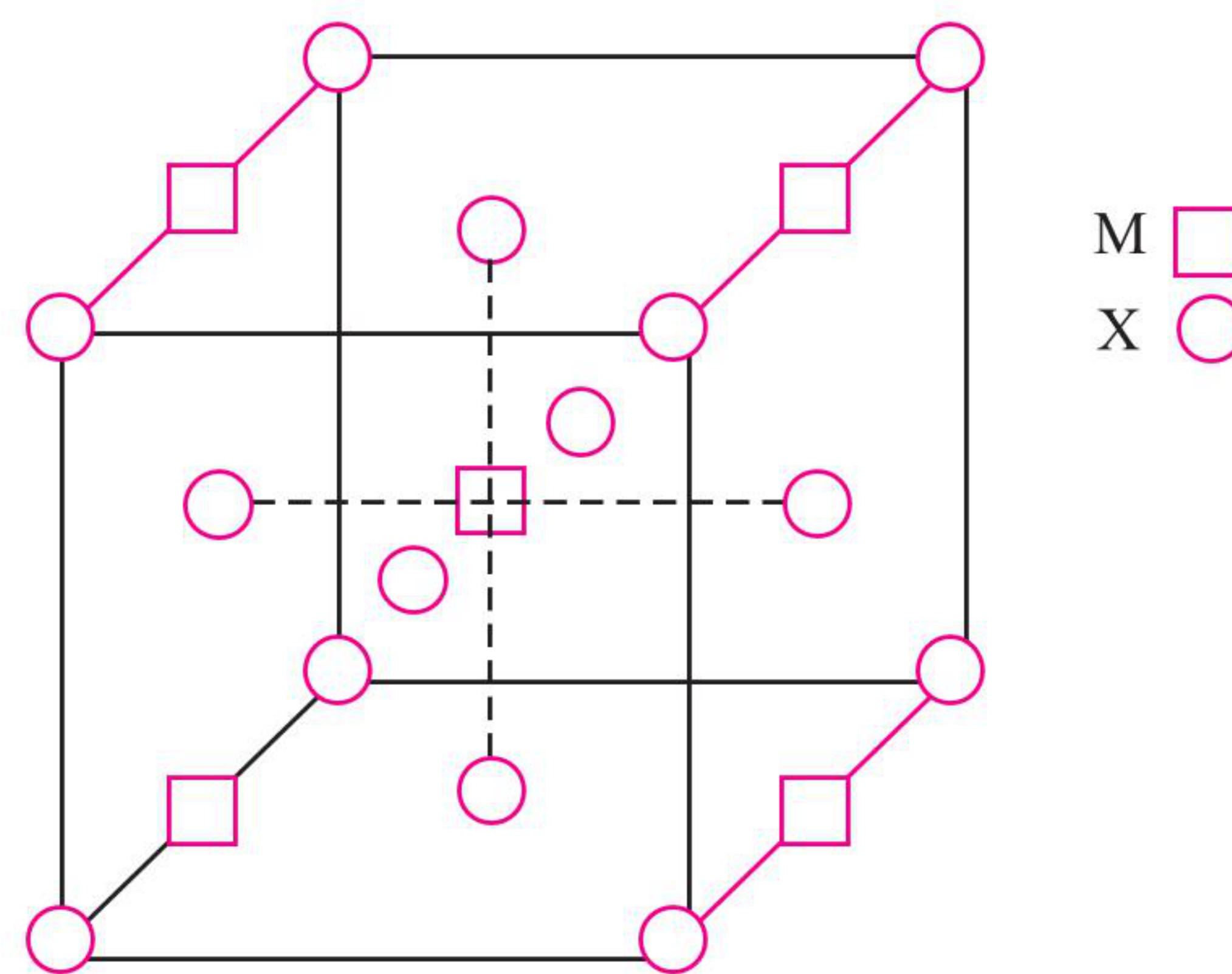
1. The packing efficiency of a two-dimensional square unit cell shown below is



- (1) 39.27%
 (2) 68.02%
 (3) 74.05%
 (4) 78.54%

(IIT-JEE, 2010)

2. A compound M_pX_q has cubic close packing (ccp) arrangement of X. Its unit cell structure is shown below. The empirical formula of the compound is



- (1) MX
 (2) MX_2
 (3) M_2X
 (4) M_5X_{14}

(IIT-JEE-2012)

3. Experimentally it was found that a metal oxide has formula $\text{M}_{0.98}\text{O}$. Metal M, is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be :

- (1) 4.08%
 (2) 6.05%
 (3) 5.08%
 (4) 7.01%

(JEE Advanced, 2013)

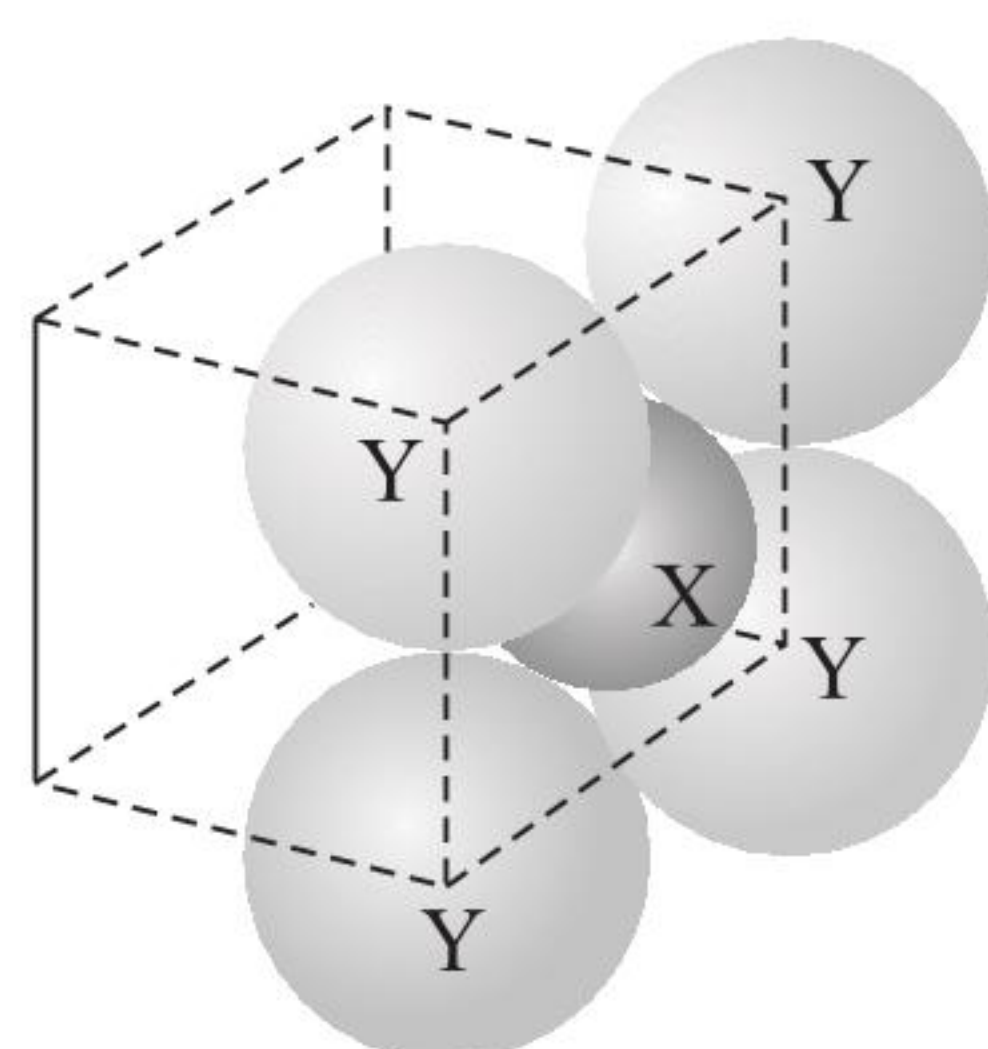
4. If the unit cell of a mineral has cubic close packed (ccp) array of oxygen atoms with m fraction of octahedral holes occupied by aluminum ions and n fraction of tetrahedral holes occupied by magnesium ions, m and n , respectively, are

- (1) $\frac{1}{2}, \frac{1}{8}$ (2) $1, \frac{1}{4}$
 (3) $\frac{1}{2}, \frac{1}{2}$ (4) $\frac{1}{4}, \frac{1}{8}$

(JEE Advanced, 2015)

5. For the given close packed structure of a salt made of cation X and anion Y shown below (ions of only one face are shown for clarity), the packing fraction is approximately (packing

$$\text{fraction} = \frac{\text{packing efficiency}}{100})$$



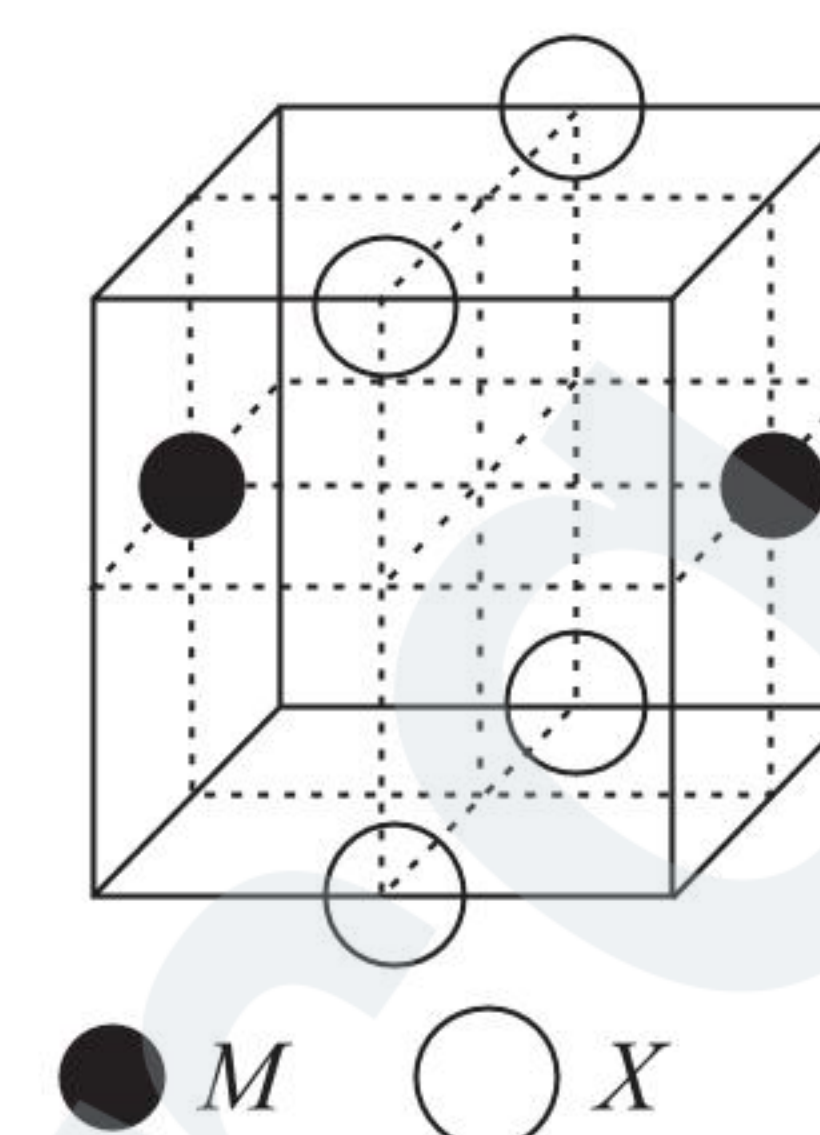
- (1) 0.74 (2) 0.63
 (3) 0.52 (4) 0.48

(JEE Advanced, 2021)

Multiple Correct Answers Type

- Which of the following statements regarding defects in solids is/are correct?
 - Frenkel defect is usually favoured by a very small difference in the sizes of cation and anion.
 - Frenkel defect is a dislocation defect.
 - Trapping of an electron in the lattice leads to the formation of F-centre.
 - Schottky defects have no effect on the physical properties of solids. (IIT-JEE 2009)
- The CORRECT statement(s) for cubic close packed (ccp) three dimensional structure is(are)
 - The number of the neighbours of an atom present in the topmost layer is 12.
 - The efficiency of atom packing is 74%.
 - The number of octahedral and tetrahedral voids per atom are 1 and 2 respectively.
 - The unit cell edge length is $2\sqrt{2}$ times the radius of the atom. (JEE Advanced, 2016)

3. The cubic unit cell structure of a compound containing cation M and anion X is shown below. When compared to the anion, the cation has smaller ionic radius. Choose the correct statement(s).



- The empirical formula of the compound is MX .
- The cation M and anion X have different coordination geometries.
- The ratio of $M-X$ bond length to the cubic unit cell edge length is 0.866.
- The ratio of the ionic radii of cation M to anion X is 0.414.

(JEE Advanced, 2020)

Numerical Value Type

- Find the number of hexagonal faces that are present in a truncated octahedral. (IIT-JEE 2011)
- A crystalline solid of a pure substance has a face-centred cubic structure with a cell edge of 400 pm. If the density of the substance in the crystal is 8 g cm^{-3} , then the number of atoms present in 256 g of the crystal is $N \times 10^{24}$. The value of N is (JEE Advanced 2017)
- Consider an ionic solid MX with NaCl structure. Construct a new structure (Z) whose unit cell is constructed from the unit cell of MX following the sequential instructions given below. Neglect the charge balance.
 - Remove all the anions (X) except the central one
 - Replace all the face centered cations (M) by anions (X)
 - Remove all the corner cations (M)
 - Replace the central anion (X) with cation (M)

The value of $\left(\frac{\text{number of anions}}{\text{number of cations}} \right)$ in Z is _____.

(JEE Advanced 2018)

Answers Key

EXERCISES

Single Correct Answer Type

- | | | | | |
|-------------------|----------|-------------------|----------|----------|
| 1. (2) | 2. (4) | 3. (2) | 4. (1) | 5. (3) |
| 6. (4) | 7. (2) | 8. (2) | 9. (1) | 10. (4) |
| 11. (3) | 12. (3) | 13. (2) | 14. (2) | 15. (3) |
| 16. (4) | 17. (1) | 18. (3) | 19. (3) | 20. (4) |
| 21. (2) | 22. (2) | 23. (4) | 24. (1) | 25. (2) |
| 26. (2) | 27. (2) | 28. (1) | 29. (2) | 30. (2) |
| 31. (3) | 32. (2) | 33. (4) | 34. (3) | 35. (3) |
| 36. (4) | 37. (4) | 38. (2) | 39. (2) | 40. (3) |
| 41. (2) | 42. (1) | 43. (1) | 44. (2) | 45. (1) |
| 46. (2) | 47. (2) | 48. (2) | 49. (2) | 50. (1) |
| 51. (1) | 52. (1) | 53. (2) | 54. (1) | 55. (3) |
| 56. (4) | 57. (2) | 58. (2) | 59. (3) | 60. (2) |
| 61. (4) | 62. (2) | 63. (1) | 64. (1) | 65. (3) |
| 66. (2) | 67. (4) | 68. (2) | 69. (2) | 70. (1) |
| 71. (3) | 72. (4) | 73. (2) | 74. (1) | 75. (3) |
| 76. (3) | 77. (3) | 78. (3) | 79. (4) | 80. (3) |
| 81. (1) | 82. (2) | 83. (4) | 84. (2) | 85. (4) |
| 86. (4) | 87. (2) | 88. (4) | 89. (2) | 90. (4) |
| 91. (2) | 92. (1) | 93. (2) | 94. (1) | 95. (3) |
| 96. (2) | 97. (3) | 98. (2) | 99. (2) | 100. (3) |
| 101. (1) | 102. (2) | 103. (4) | 104. (2) | 105. (2) |
| 106. (3) | 107. (3) | 108. (4) | 109. (2) | 110. (2) |
| 111. (4) | 112. (1) | 113. (1) | 114. (3) | 115. (2) |
| 116. (4) | 117. (1) | 118. (3) | 119. (2) | 120. (3) |
| 121. (4) | 122. (3) | 123. (2) | 124. (2) | 125. (2) |
| 126. (4) | 127. (3) | 128. (1) | 129. (2) | 130. (3) |
| 131. (2) | 132. (2) | 133. (2) | 134. (1) | 135. (3) |
| 136. (2) | 137. (1) | 138. (2) | 139. (3) | 140. (2) |
| 141. (1) | 142. (1) | 143. (1) | 144. (2) | 145. (1) |
| 146. (2) | 147. (2) | 148. (2) | 149. (1) | 150. (2) |
| 151. (1, 3, 4) | | 152. (1, 2, 3, 4) | | |
| 153. (1, 2, 3, 4) | | 154. (3) | 155. (2) | 156. (2) |
| 157. (2) | 158. (1) | 159. (2) | 160. (3) | 161. (3) |
| 162. (2) | 163. (1) | 164. (4) | 165. (1) | |

Multiple Correct Answers Type

- | | | |
|------------------|---------------|------------------|
| 1. (1, 3) | 2. (1, 4) | 3. (3, 4) |
| 4. (1, 2, 4) | 5. (1, 3) | 6. (2, 4) |
| 7. (1, 4) | 8. (1, 2, 3) | 9. (1, 2, 3, 4) |
| 10. (1, 2, 3) | 11. (1, 2) | 12. (1, 2, 3, 4) |
| 13. (1, 2, 3, 4) | 14. (2, 3) | 15. (1, 3) |
| 16. (1, 4) | 17. (1, 2, 4) | 18. (1, 2, 4) |
| 19. (1, 2, 3, 4) | 20. (1, 2, 3) | 21. (1, 2, 3) |
| 22. (2, 4) | 23. (2) | 24. (1, 2, 3, 4) |
| 25. (1, 3) | 26. (3, 4) | 27. (2, 3, 4) |

- | | | |
|------------------|------------------|------------------|
| 28. (1, 4) | 29. (1, 2, 4) | 30. (2, 3) |
| 31. (1, 3, 4) | 32. (1, 2, 3, 4) | 33. (1, 2) |
| 34. (2, 3) | 35. (1, 2, 3) | 36. (1, 2, 3, 4) |
| 37. (1, 3) | 38. (1, 2, 3) | 39. (3, 4) |
| 40. (2, 3) | 41. (1, 2, 3) | 42. (1, 2, 3) |
| 43. (1, 2, 3, 4) | 44. (1, 2, 3, 4) | 45. (2, 3, 4) |
| 46. (1, 2, 3, 4) | 47. (1, 2, 3, 4) | 48. (1, 2, 4) |
| 49. (1, 2, 3, 4) | 50. (1, 3, 4) | 51. (1, 2, 3, 4) |
| 52. (1, 2, 3) | 53. (1, 4) | 54. (2, 3) |
| 55. (1, 2, 4) | 56. (1, 2) | 57. (1, 4) |
| 58. (1, 2, 3) | | |

Linked Comprehension Type

- | | | | | |
|---------|---------|--------|--------|---------|
| 1. (1) | 2. (3) | 3. (2) | 4. (1) | 5. (3) |
| 6. (4) | 7. (1) | 8. (3) | 9. (3) | 10. (1) |
| 11. (2) | 12. (4) | | | |

Matrix Match Type

Q. No.	a	b	c	d	e	f	g
1.	q, r, s	p, r, s	r	—	—	—	—
2.	s	p	q	r	—	—	—
3.	q	p	s	r	t	—	—
4.	q	r	p	s	t	—	—
5.	r	p	s	q	u	t	—
6.	q	r	p	u	s	t	—

- | | | | |
|--------|--------|--------|---------|
| 7. (1) | 8. (4) | 9. (2) | 10. (4) |
|--------|--------|--------|---------|

Numerical Value Type

- | | | | | |
|---------|--------|--------|--------|----------|
| 1. (7) | 2. (2) | 3. (2) | 4. (4) | 5. (7) |
| 6. (6) | 7. (8) | 8. (2) | 9. (8) | 10. (13) |
| 11. (4) | | | | |

ARCHIVES

JEE Advanced

Single Correct Answer Type

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (4) | 2. (2) | 3. (1) | 4. (1) | 5. (2) |
|--------|--------|--------|--------|--------|

Multiple Correct Answers Type

- | | | |
|-----------|--------------|-----------|
| 1. (2, 3) | 2. (2, 3, 4) | 3. (1, 3) |
|-----------|--------------|-----------|

Numerical Value Type

- | | | |
|--------|--------|--------|
| 1. (8) | 2. (2) | 3. (3) |
|--------|--------|--------|

Solutions

Chapter 1

Concept Application Exercises

Exercise 1.1

1. There are two alternate faces of a cube

(a) Face centre share = $2 \times \frac{1}{2} = 1$

(b) Corner share = $8 \times \frac{1}{8} = 1$

$\therefore$ Formula = XY

2. There are 4 diagonals of a cube.

$\therefore$ Diagonals are in body centre and does not share.

Diagonal share = $4 \times 2 = 8$

Corner share = $8 \times \frac{1}{8} = 1$

$Z_{\text{eff}} = 9$

3. Number of A atom:

Corners share = $8 \times \frac{1}{8} = 1$

Face centre share = $6 \times \frac{1}{2} = 3$

Total = 4

Number of B atoms;

Body centre share = 1

Edge centre share = $12 \times \frac{1}{4} = 3$

Total = 4

Formula: $A_4B_4 = 4AB$

4. Corner share = $7 \times \frac{1}{8} = \frac{7}{8}$

Face centre share = $6 \times \frac{1}{2} = 3$

Formula: $A_{7/8}B_3$ or A_7B_{24} .

5. In NaCl, it has 6 : 6 CN

$\therefore$ It has OV.

$\therefore r = \frac{r_{\ominus}}{0.414} = \frac{100}{0.414} = 241 \text{ pm}$

6. Let number of anion $B^{\ominus} = 1/\text{atom}$

Number of TV = 2/atom

Number of OV = 1/atom

(2 TVs are present above and below each sphere and 1 OV per atom is present in midway between the two close-packed layers).

Number of cation $A^{\oplus} = 2$

(Since cation A is equally distributed between OV and TV).

Formula: A_2B .

7. Let number of anion (O^{2-}) = 1/atom

Number of TV = 2/atom

Number of OV = 1/atom

Number of cation (Al^{3+}) = $\frac{2}{3} \times 1 = \frac{2}{3}$

Formula: $Al_{2/3}^{3+} O^{2-}$ or Al_2O_3 .

8. (a) M_w of $NH_4Cl = 53.5$

$Z_{\text{eff}} = 1$

$a^3 = \frac{53.5 \times 1}{1.534 \times 6.023 \times 10^{23}} = 5.79 \times 10^{-23} \text{ cm}$

$a = 3.87 \times 10^8 \times 10^{10} \text{ pm} = 387 \text{ pm}$

- (b) (CsCl type) (bcc type)

For atoms $\left[r = \frac{\sqrt{3}}{4} a \right]$

For ionic compound $[2(r_{\oplus} + r_{\ominus})]^2 = 3a^2$

$2(r_{\oplus} + r_{\ominus}) = \sqrt{3}a$

$(r_{\oplus} + r_{\ominus}) = \frac{\sqrt{3}}{2} a = \sqrt{3} \times 387/2 = 335.1 \text{ pm}$

- (c) $r_{\oplus} + r_{\ominus} = 335.1 \text{ pm}$

$r_{\oplus} = 335.1 - r_{\ominus}$
 $= 335.1 - 181 = 154.1 \text{ pm}$

9. NaCl has fcc-type structure. The ideal limiting radius ratio is 0.414.

$\frac{r_{\oplus}}{r_{\ominus}} = 0.414$

$r_{\ominus} = \frac{90}{0.414} = 217.4 \text{ pm}$

When the structure is not ideally close packed (i.e., anions do not touch each other) the limiting ratio can be upto 0.73.

Minimum radius of anion = $\frac{r_{\oplus}}{0.73} = \frac{90}{0.73} = 123.3 \text{ pm}$

10. Limiting radius ratio = $\frac{r_{\oplus}}{r_{\ominus}}$

In NaCl crystal, $Cl^{\ominus}$ forms cubic close packing and $Na^{\oplus}$ ions occupy all OVs.

For a cation to fit exactly in OV,

$\frac{r_{\oplus}}{r_{\ominus}} = 0.414$

$r_{\oplus} = 0.414 r_{\ominus}$

Ideal radius for cation = $0.414 \times 250 = 103.5 \text{ pm}$

For a TV,

$\frac{r_{\oplus}}{r_{\ominus}} = 0.225$

Ideal radius for the cation = $0.225 r_{\ominus}$
 $= 0.225 \times 250 = 56.25 \text{ pm}$

Since the size of the cation (180 pm) is much larger than the ideal radius (56.25 pm), the cation introduced in TV of the crystal, pushes the anions outwards and the anions do not remain close packed. The new structure will be unstable.

11. Let number of $O^{2-} = 1/\text{atom}$

Number of TV = 2/atom

Number of TV = 1/atom

$$\text{Number of } A^{2+} = \frac{1}{8} \times 2 = \frac{1}{4}$$

$$\text{Number of } B^{3+} = \frac{1}{2} \times 1 = \frac{1}{2}$$

Formula: $A_{1/4}^{2+}B_{1/2}^{3+}O^{2-}$ or AB_2O_4 .

12. (a) NaCl-type structure

i. It means 6 : 6 coordination

$$\therefore \text{CN of } Mg^{2+} = 6$$

$$\text{CN of } O^{2-} = 6$$

ii. CsCl-type structure.

It means CN = 8 : 8.

$$\therefore \text{CN of } Tl^{\oplus} = 8$$

$$\text{CN of } Cl^{\ominus} = 8$$

(b) For close-packed XY type solid,

The radius ratio ($r_{\oplus}/r_{\ominus}$) lies in the range of 0.414–0.732.

$$\therefore \text{Minimum value of } r_{\ominus} = \frac{r_{\oplus}}{0.732} = \frac{73.2}{0.732} \text{ pm} = 100 \text{ pm}$$

$$\text{Maximum value of } r_{\ominus} = \frac{r_{\oplus}}{0.414} = \frac{73.2}{0.414} \text{ pm} = 176.81 \text{ pm}$$

(c) $\frac{r_{Fe^{3+}}}{r_{O^{2-}}} = \frac{0.7}{1.4} \text{ \AA} = 0.5$ which lies in the range of 0.414–0.732.

Hence, Fe^{3+} ion will be in OV's.

(d) (Refer Section 1.16.4)

For bcc-type (CsCl) structure

$$r_{\oplus} + r_{\ominus} = \frac{\sqrt{3}}{2} a = \frac{1.732}{2} \times 400 \text{ pm} = 346.4 \text{ pm}$$

13. a. Stoichiometric formula should be (AB type, NaCl type) = CdO.

Non-stoichiometric formula = $CdO_{0.95}$.

Since CdO is NaCl type (fcc type), anion (O^{2-}) forms fcc arrangement.

$$\text{Number of anionic vacant sites} = 1 - 0.95 = 0.05$$

$$\% \text{ of anionic vacant sites} = 0.05 \times 100 = 5\%$$

b. M_w of non-stoichiometric $CdO_{0.95} = [112.41 + 0.95 \times 16] = 127.61 \text{ g mol}^{-1}$

Z_{eff} for fcc type = 4

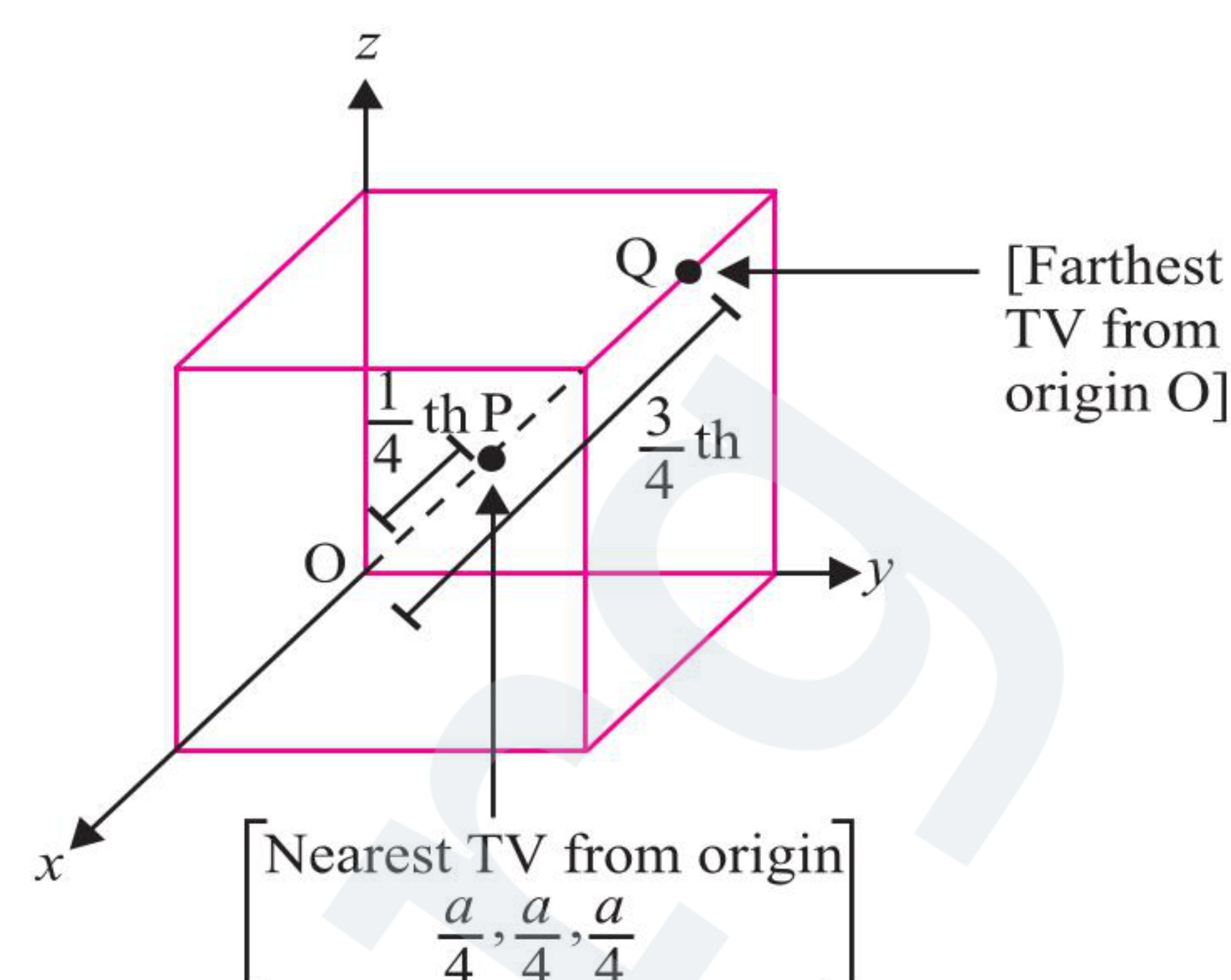
$$\rho = \frac{Z_{\text{eff}} \times M_w}{N_A \times a^3} = \frac{4 \times 127.61 \text{ g mol}^{-1}}{6.023 \times 10^{23} \times (470 \times 10^{-10})^3} = 8.21 \text{ g cm}^{-3}$$

c. M_w of stoichiometric CdO = $(112.41 + 16) = 128.41 \text{ g mol}^{-1}$

$$\rho = \frac{4 \times 128.41 \text{ g mol}^{-1}}{6.023 \times 10^{23} \times (470 \times 10^{-10})^3} = 8.26 \text{ g cm}^{-3}$$

14. a. The centers of TVs lie 1/4th distance of the body diagonal. But the coordinates are 1/4th of a . Hence, coordinates of TVs

nearest to origin in x , y , and z direction are: $\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ as shown:



Hence, coordinates of TVs farthest to origin in x , y , z direction are:

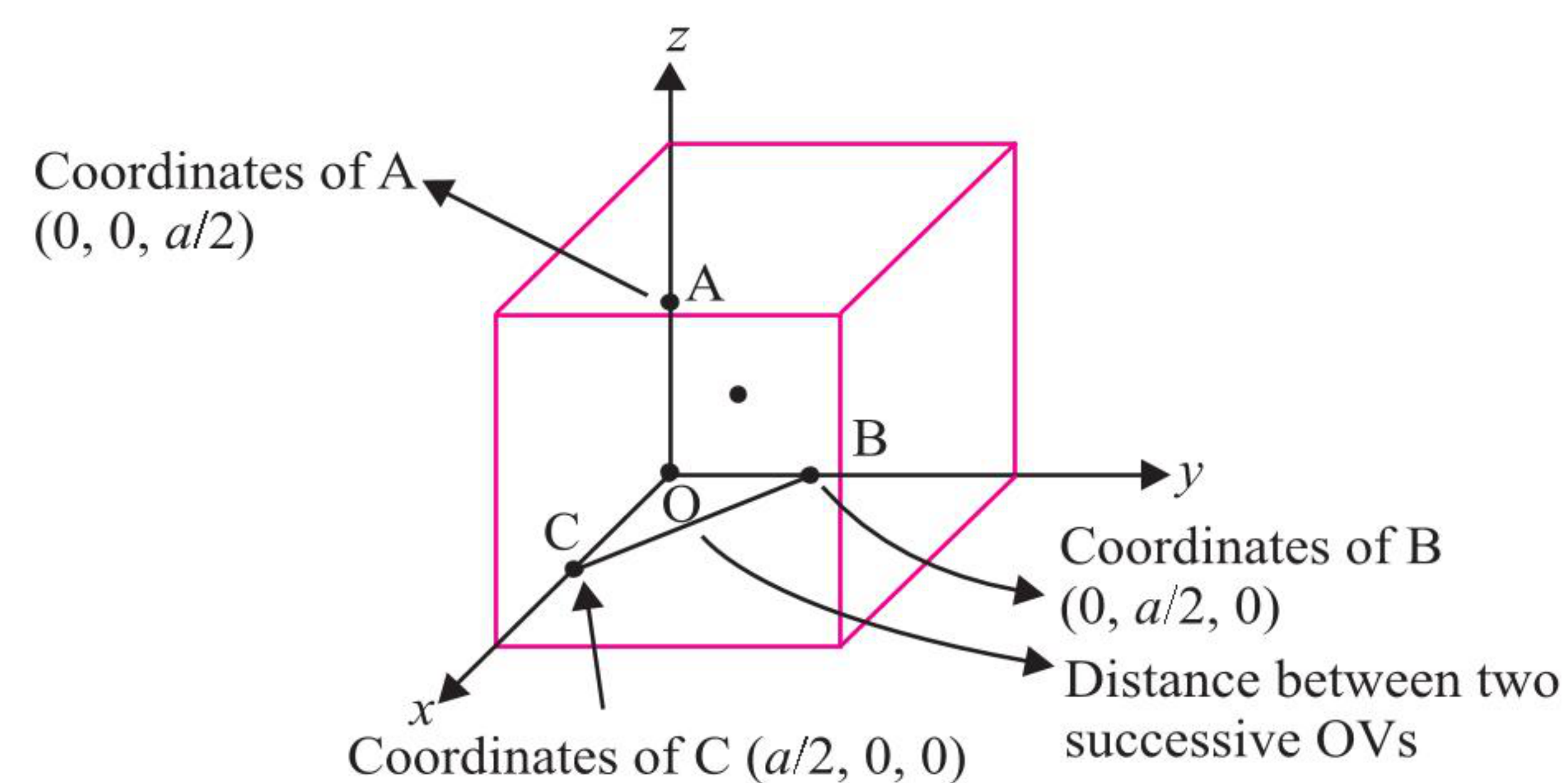
$$\left(\frac{3a}{4}, \frac{3a}{4}, \frac{3a}{4}\right)$$

b. Distance between two successive TVs

Distance between $P\left(\frac{a}{4}, \frac{a}{4}, \frac{a}{4}\right)$ and $Q\left(\frac{3a}{4}, \frac{3a}{4}, \frac{3a}{4}\right)$ is $a/2$.

c. OV's are formed on body center and edge centers.

A, B, C are OV's at edge centers on z , y , and x axis, respectively.



i. Hence, coordinates of OV's nearest to origin are:

$$\left(0, \frac{a}{2}, 0\right), \left(\frac{a}{2}, 0, 0\right), \left(0, 0, \frac{a}{2}\right)$$

ii. To get the farthest OV's from origin, we have to cover distance equal to the side of the cube on x , y , z axes.

For x -axis, coordinates are: $x = a/2, y = a, z = a$.

For y -axis, coordinates are: $x = a, y = a/2, z = a$

For z -axis, coordinates are: $x = a, y = a, z = a/2$

Hence, coordinates of OV's farthest to origin are:

$$\equiv \left(\frac{a}{2}, a, a\right); \left(a, \frac{a}{2}, a\right); \left(a, a, \frac{a}{2}\right)$$

d. Distance between any two points

$$= \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2}$$

Coordinates of OV's nearest to origin are:

$$\left(0, \frac{a}{2}, 0\right); \left(\frac{a}{2}, 0, 0\right); \left(0, 0, \frac{a}{2}\right)$$

Hence, distance between two successive OV's

$$= \sqrt{\left(\frac{a}{2} - 0\right)^2 + \left(0 - \frac{a}{2}\right)^2 + (0 - 0)^2} = \frac{a}{\sqrt{2}}$$

Alternatively

Distance between two successive OVs
= Distance between body center and any
edge center of the fcc unit cell.

$$= \frac{a}{\sqrt{2}}$$

Exercise 1.2

1. The number of Schottky defects (n) is given as:

$$n = Ne^{-E/2KT} \quad \dots(i)$$

$$\text{Number of moles of ions} = \text{Number of moles of Schottky defects} \\ = \frac{N}{N_A}$$

Mole fraction of defect (X) is given as:

$$X = \frac{n/N_A}{n/N_A + N/N_A} = \left(\frac{n}{n + N} \right) = \left(\frac{n/N}{N/N + 1} \right)$$

From Eq. (i)

$$X = \left(\frac{e^{-E/2KT}}{e^{-E/2KT} + 1} \right)$$

(Since $E = \Delta H = 2 \text{ eV} = 2 \times 1.608 \times 10^{-19} \text{ J}$)

$\therefore$ The value of $E/2KT$ is

$$= \frac{2 \times 1.608 \times 10^{-19} \text{ J}}{2 \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 2900 \text{ K}} \\ \approx 4$$

$\therefore X = e^{-4}/(e^{-4} + 1)$ (The value of $e = 2.7$)

$$\Rightarrow \frac{(2.7)^{-4}}{(2.7)^{-4} + 1} = \frac{0.018}{0.018 + 1}$$

$$\therefore X = \frac{0.018}{1.018} = 0.0176$$

Taking $(-\ln)$ of both sides

$$\therefore -\ln X = -\ln(0.0176)$$

$$\Rightarrow -\ln X \approx 4$$

2. (a) The compound is $\text{Fe}_{0.95}\text{O} \equiv \text{Fe}_{95}\text{O}_{100}$.

Let the compound has $x\%$ of Fe^{2+} and $(95 - x)\%$ of Fe^{3+} ion.

For electrical neutrality:

Total positive charge = Total negative charge

$$2x + 3(95 - x) = 2 \times 100 \Rightarrow x = 85\%$$

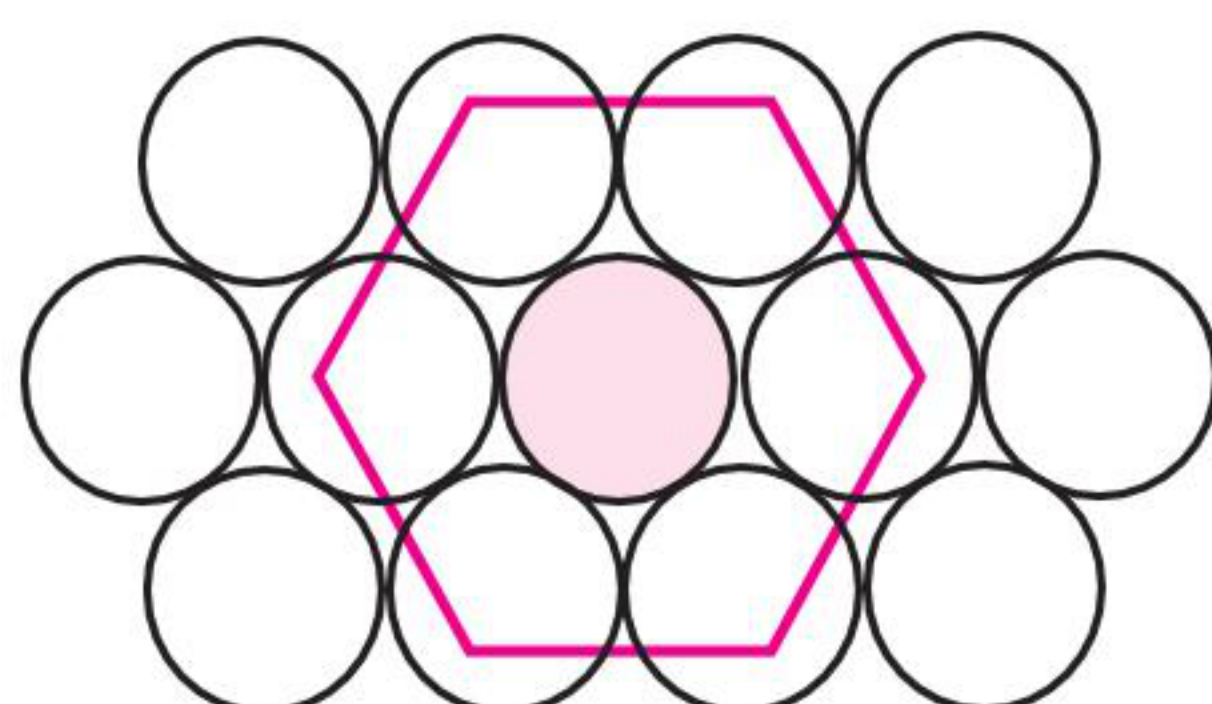
Thus, $\text{Fe}^{2+} = 85\%$ and $\text{Fe}^{3+} = (95 - 85) = 10\%$

$$\text{Hence, } \frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} = \frac{85}{10} = 8.5$$

- (b) Number of vacant sites = $100 - 95 = 5\%$

3. (i) $a = 2R$, where a is the length of the side of parallelogram and R is the radius of circle.

- (ii) The crystal coordination number (CN) is the number of nearest neighbours around a given atom, ion or molecular on the crystal, as shown below:



From the figure, each atom is touching six other atoms so, $\text{CN} = 6$

4. (i) Maximum radius ratio in ionic crystal lies in the range $0.732 - 1$ which corresponds to a coordination number of 8. Hence, coordination number greater than 8 is not possible in ionic crystals.

- (ii) CsCl is more stable than NaCl. This is because higher the coordination number, greater are the forces of attraction between the cations and the anions in the close-packed arrangement. As CsCl has co-ordination number of $8 : 8$ while NaCl has a coordination number of $6 : 6$, therefore CsCl is more stable

5. (i) Frenkel defects are found in silver halides (AgCl , AgBr and AgI) due to small size of $\text{Ag}^{\oplus}$ ion. It is also shown by ZnS due to small size of Zn^{2+} ion. They are not found in alkali metal halides as the alkali metal ions cannot fit into the interstitial sites.

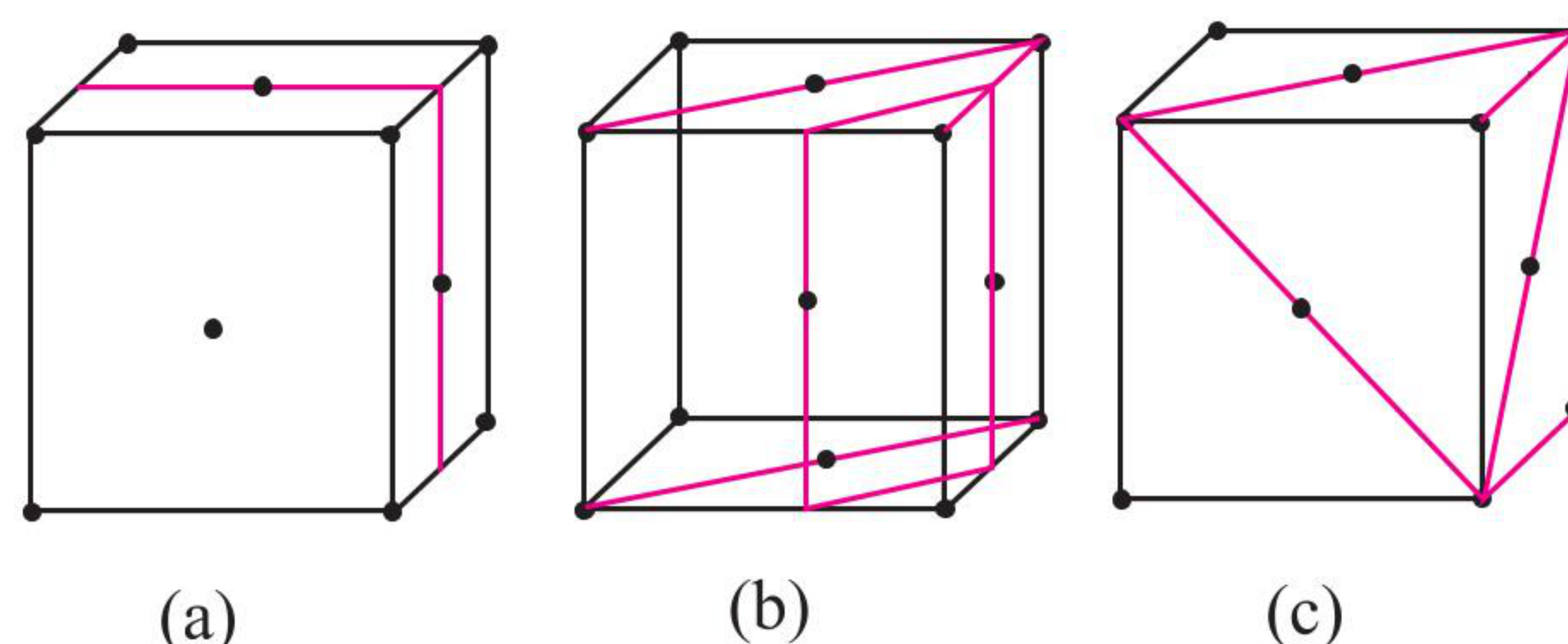
- (ii) As the number of ions decreases as a result of this defect, the mass decreases whereas the volume remains the same.

Hence, like vacancy defect, the density of the solid decreases. It is observed that in NaCl crystal at room temperature, there are about 10^{22} ions and 10^6 Schottky pairs per cm^3 . This means that there is one Schottky pair defect per 10^{16} ions. Thus, there are large number of holes present in the crystal. This result in the decrease in the density.

6. (a) Levitation occurs when objects float in air due to the mutual repulsion between permanent magnet and a super conductor.

- (b) H. Kamerlingh-Onnes found that down to 4.15 K , the resistance of mercury decreased with decrease in temperature as is the case with most metals. However, fell sharply close to zero. Thus, at or below the critical temperature, mercury became a superconductor.

7. Using Bragg's law, $n\lambda = 2d \sin \theta$, and assuming that the diffractions are of first order ($n = 1$), the distance are calculated to be 0.204 nm , 0.176 nm and 0.124 nm . The distance 0.176 nm is seen to be half the unit cell length, corresponding to the perpendicular distance between layers of atoms in one face of the unit cell and the center. The distance 0.204 nm turns out to be $1/\sqrt{3}$ times the unit cell length, corresponding to the perpendicular distance between a corner of the unit cell and the plane of the three adjacent corners. The distance 0.124 nm corresponds to $\sqrt{2}/4$ times the unit cell dimension—one fourth of the distance from one edge of the cell to the opposite edge. The plane intersects the face-centered atoms of two sides. The plane including the edge atoms is equivalent to the plane across the centre of the unit cell.



8. CrO_2 is used to make magnetic tapes used for audio recording and it is ferromagnetism. Such substances remain permanently magnetised, only they have been magnetised.

9. Fraction of edge unoccupied = $\frac{a - 2R}{a}$

$$a = 2\sqrt{2}R, \quad X = \frac{2(\sqrt{2} - 1)}{2\sqrt{2}} \quad (\sqrt{2} = 1.414)$$

$$X = \frac{0.414}{1.414} = 0.293$$

$$Z = \frac{X}{0.097} = \frac{0.293}{0.097} = 3$$

10. NaA is salt of S_B/W_A

$$\text{pH} = \frac{pK_w}{2} + \frac{1}{2}(pK_a + \log c)$$

$$8 = 6.5 \times \frac{1}{2}(5 + \log c)$$

$$1.5 \times 2 = 5 + \log c$$

$$\log c = -2$$

$$\therefore c = 0.01 \text{ mol L}^{-1}$$

$$\therefore M = \frac{W_2}{Mw_2 \times \text{Vol. of soln. in litre}}$$

$$= \frac{2.592}{0.01 \times 2} = 129.6$$

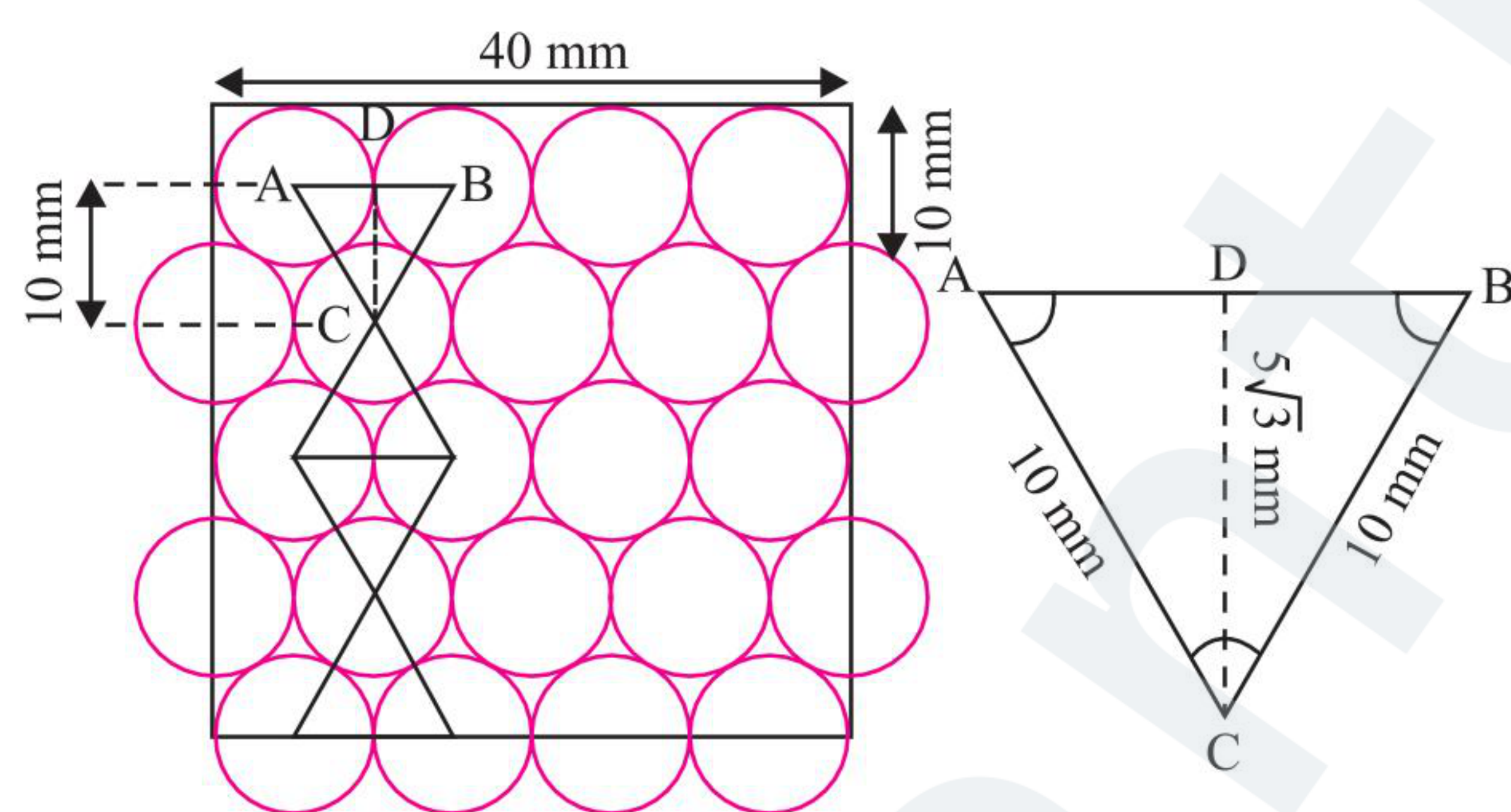
$$\rho = \frac{Z_{\text{eff}} \times Mw_2}{NA \times a^3 \times 10^{-30}} \quad (Z_{\text{eff}} = 4) \quad (a = 2 \times 300 = 600 \text{ pm})$$

$$\rho = \frac{4 \times 129.6}{6 \times 10^{23} \times (600)^3 \times 10^{-30}} = 4 \text{ g cm}^{-3}$$

11. $Z = 4 + 6 + 6 + 12 + 12 = 40$

$$\frac{Z}{20} = \frac{40}{20} = 2$$

12.



$$CD = 10 \sin 60 = 10 \frac{\sqrt{3}}{2}$$

$$= 5\sqrt{3} \text{ mm}$$

Area of square having spherical marbles in it

$$= 40 \times 10^{-1} \times 40 \times 10^{-1} \text{ cm}^2 = 16 \text{ cm}^2$$

The maximum number of sphere of 10 mm diameter in hcp packing can be seen in the figure above.

Total length covered by spheres = $5 + 4 \times CD$

$$= 5 + 4 \times 10 \sin 60^\circ$$

$$= 5 + 4 \times 5\sqrt{3} = 40 \text{ mm}$$

$$\text{Maximum number of sphere(s)} = \frac{14}{(\text{Full})} + \frac{8}{(\text{Half})} = 18$$

$$\therefore \text{Number of spheres per cm}^2 = \frac{18}{16} = 1.125$$

Exercises

Single Correct Answer Type

1. (2) 2. (4) 3. (2) 4. (1) 5. (3)

6. (4) Orthorhombic contains:

Simple, Body centre, Face centre & End centre bravais lattices.

7. (2) Cubic-symmetrical

$$\alpha = \beta = \gamma \neq 90^\circ, \quad a = b = c$$

Triclinic-unsymmetrical

$$\alpha \neq \beta \neq \gamma \neq 90^\circ, \quad a \neq b \neq c$$

8. (2) Tetragonal $a = b \neq c, \quad \alpha = \beta = \gamma = 90^\circ$

9. (1) $Z = 8 \times \frac{1}{8} = 1$

Nearest neighbour = 6

10. (4) $Z = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Nearest neighbour = 12

11. (3) $Z = 8 \times \frac{1}{8} + 1 = 2$

Nearest neighbour = 8

12. (3) fcc unit cell ABCABCABC.....

Packing efficiency = 74% voids = 26%

Voids fraction = 0.260

13. (2) C.N. of A = x (B)

C.N. of B = y (A)

Formula $A_y B_x$

No. of atoms: A : B = y : x

14. (2) $\rho_1 = \frac{2 \times 56}{\left(\frac{4r}{\sqrt{3}}\right)^3}; \rho_2 = \frac{4 \times 56}{(2\sqrt{2}r)^3}$

$$\frac{\rho_1}{\rho_2} = 0.918$$

15. (3) $2.32 = \frac{2 \times Mw}{6 \times 10^{23} (1.22)^3 \times 10^{-21}} \quad (1 \text{ nm} = 10^{-9} \text{ m} = 10^{-7} \text{ cm})$

$$\Rightarrow Mw = 1264$$

$$\text{TiAl}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O} = 1264.$$

$$204 + 27 + 2 \times 96 + x \times 18 = 1264$$

$$\therefore x = 46.72 \approx 47$$

16. (4) Effective no. of atoms of B present in unit cell = 2

Total volume of B unoccupied by A in a unit cell

$$= 2 \times \frac{4}{3} (R^3 - r^3) \times \pi$$

$$= \frac{7\pi R^3}{3}$$

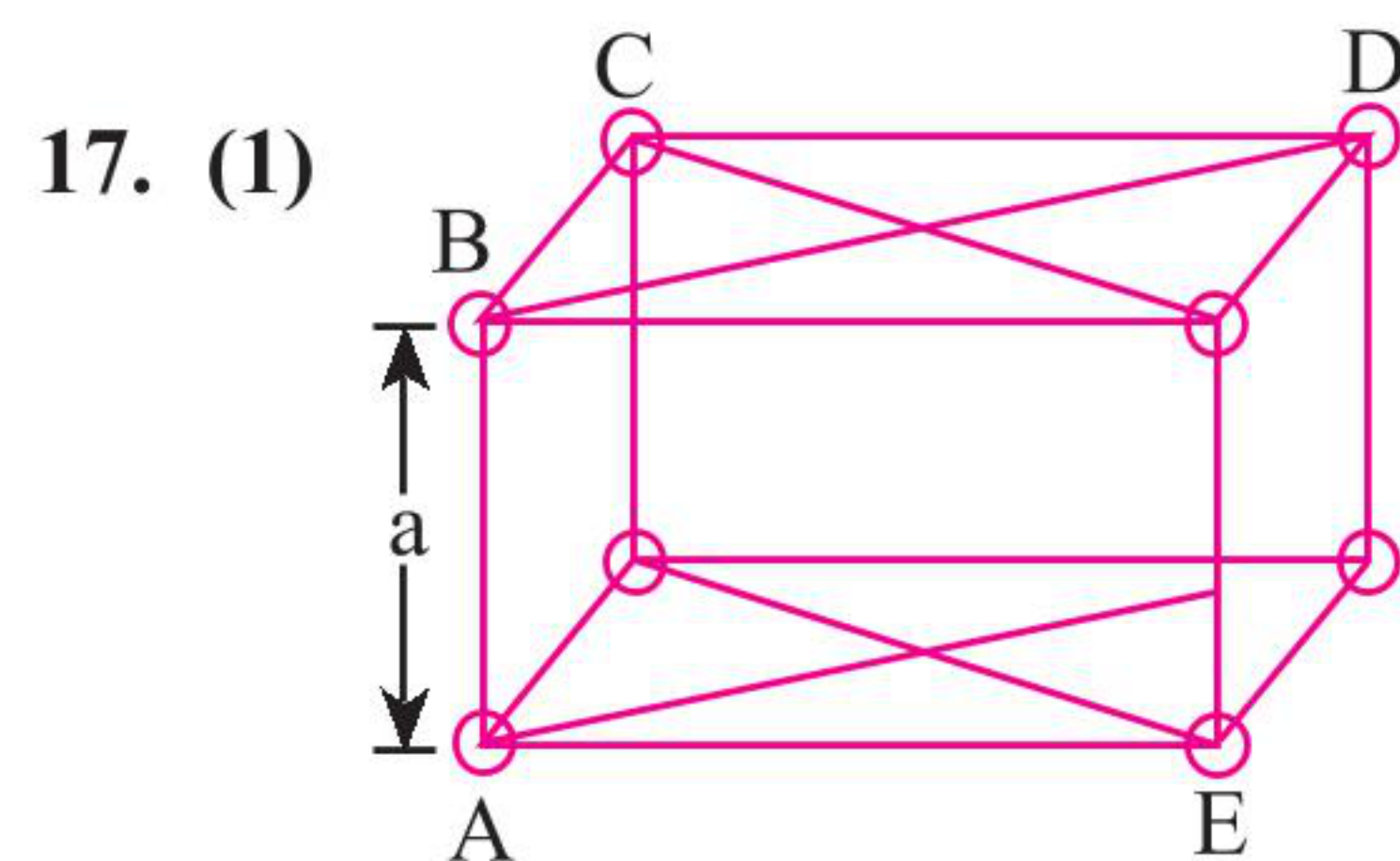
Volume of unit cell = a^3

$$\Rightarrow \left(\frac{4R}{\sqrt{3}}\right)^3 = \frac{64}{3\sqrt{3}} R^3$$

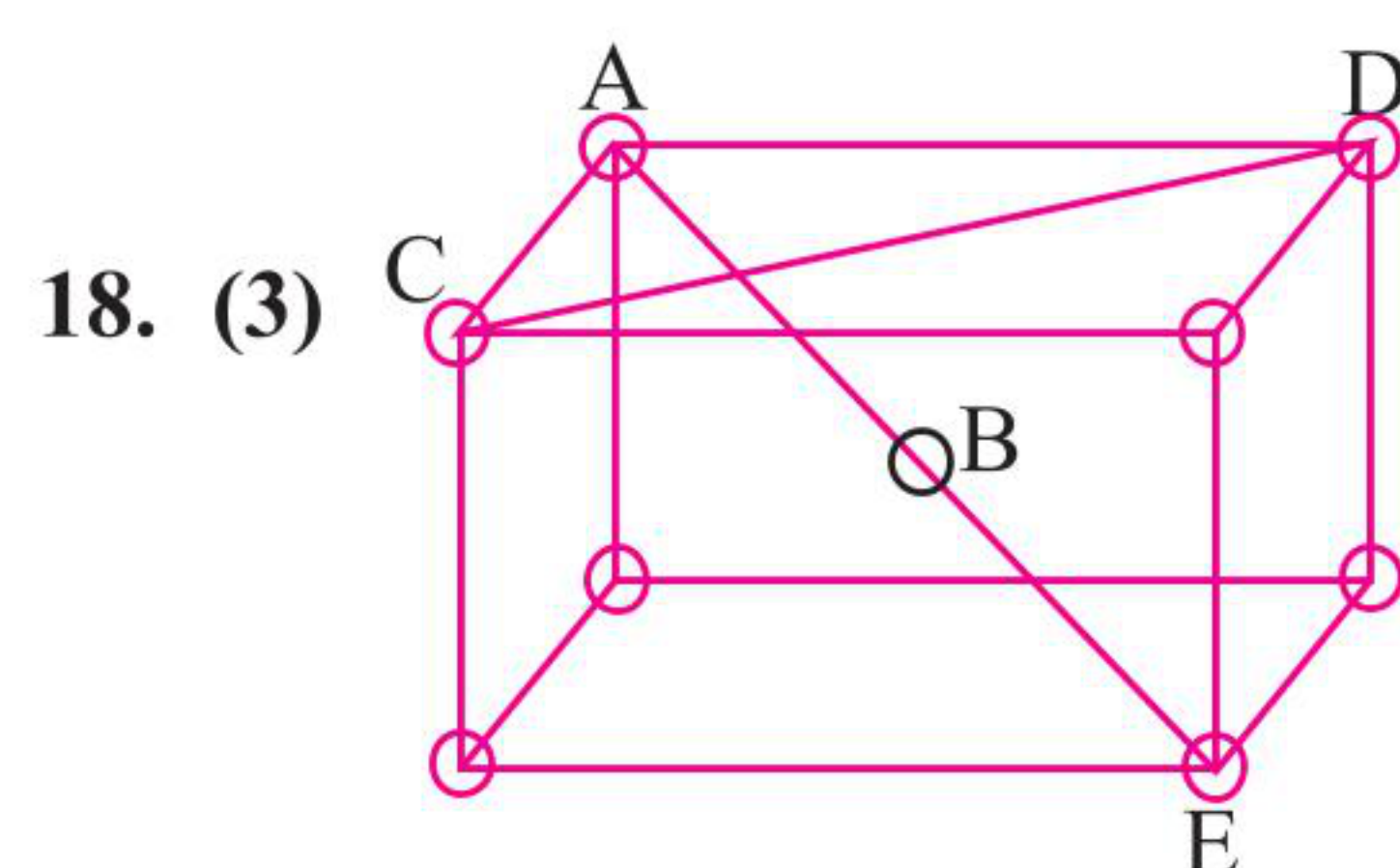
$$(\because \sqrt{3}a = 4R)$$

$$\left(\because r = \frac{R}{2}\right)$$

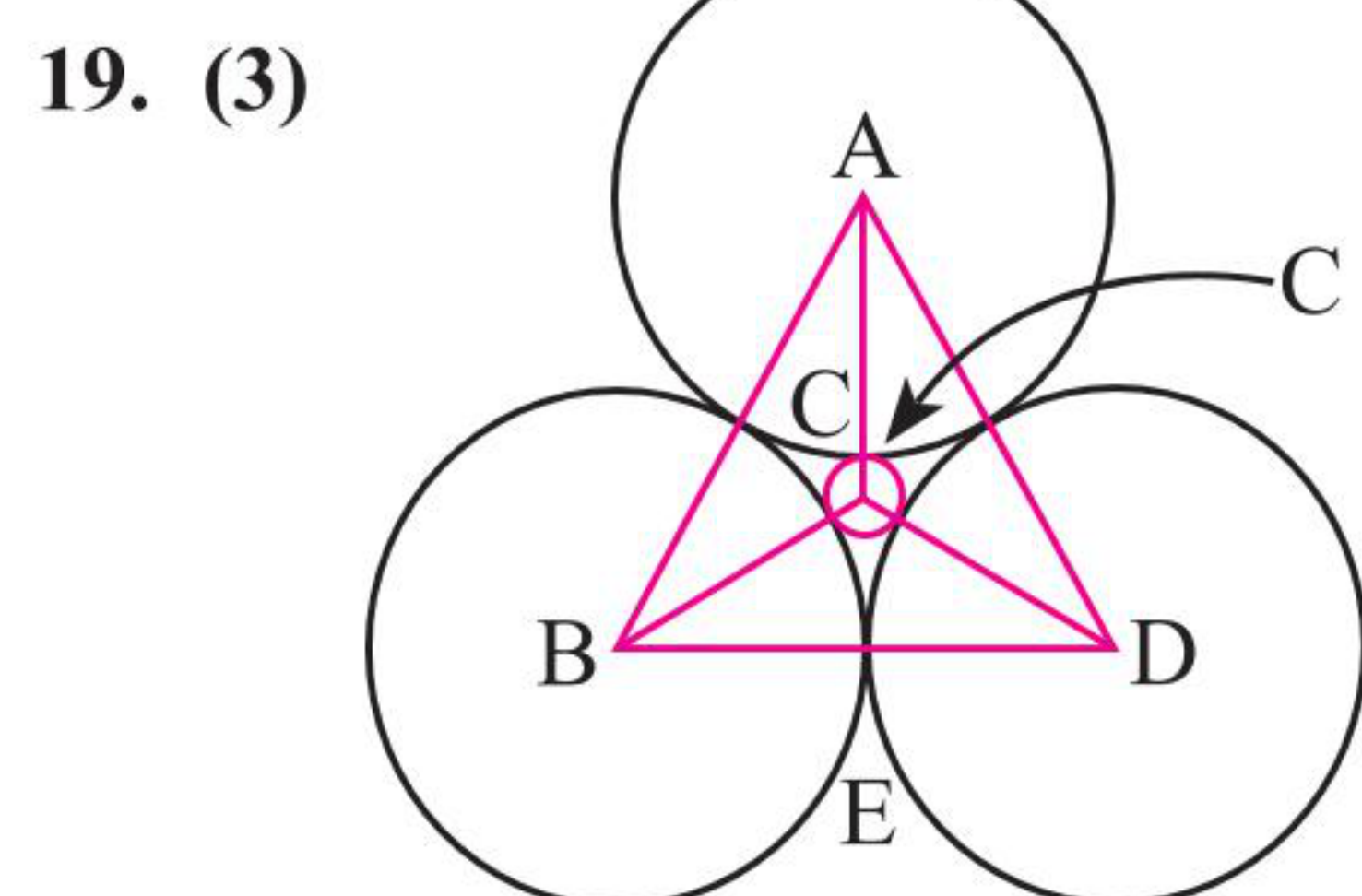
$$\text{Desired ratio} \Rightarrow \frac{\frac{7\pi R^3}{3}}{\frac{64}{3\sqrt{3}} R^3} = \frac{7\pi\sqrt{3}}{64}$$



$$\begin{aligned} AB &= a && \text{(nearest)} \\ BD &= \sqrt{2}a && \text{(next-nearest)} \\ CE &= \sqrt{3}a && \text{(next-next-nearest)} \end{aligned}$$



$$\begin{aligned} AB &= \frac{\sqrt{3}a}{2} && \text{(nearest)} \\ AC &= a && \text{(next-nearest)} \\ CD &= \sqrt{2}a && \text{(next-next-nearest)} \end{aligned}$$



$$\frac{BE}{BC} = \cos 30^\circ = \frac{\sqrt{3}}{2}$$

Distance between the centres of two B atoms

$$= 2 \times BE = \sqrt{3} \text{ \AA}$$

20. (4) Vol. of unit cell $= a^2 \sin 60^\circ \times b$
 $= 173.2 \times 10^{-24} \text{ cm}^3$

$$a = 5 \text{ \AA}$$

Mass of unit cell

$$= 173.2 \times 10^{-24} \times 5 \times 6 \times 10^{23}$$

$$= 519.6 \text{ g}$$

No. of molecules present in given unit cell

$$= \frac{519.6}{259.8} = 2$$

21. (2) In hcp arrangement total height

$$h = 4 \times \sqrt{\frac{2}{3}} r$$

as per given

$$\frac{h}{2} = 2\sqrt{\frac{2}{3}} r = 3.35 \text{ \AA} = 3.35 \times 10^{-8} \text{ cm.}$$

$$\text{Volume of unit cell} = 24 \sqrt{2} r^3$$

$$= 24\sqrt{2} \left(\sqrt{\frac{3}{2}} \times \frac{1}{2} \times 3.35 \times 10^{-8} \right)^3$$

$$= 2.93 \times 10^{-22} \text{ cm}^3$$

Effective no. of atoms in hexagonal unit cell = 6

$$\therefore \text{density} = \frac{6 \times 12}{6.023 \times 10^{23} \times 2.93 \times 10^{-22}} = 0.41 \text{ g/cc}$$

22. (2) Effective no. of $\text{Na}^{\oplus} = 4 - \left(1 + 2 \times \frac{1}{4} \right) = \frac{5}{2}$

$$\text{For } \text{Cl}^{\ominus} = 4\sqrt{2}a = 4r^{\ominus}$$

$$\text{P. F.} = \frac{\text{Vol. of effective no. of cation and anions}}{\text{Vol. of unit cell}}$$

$$= \frac{\frac{4}{3} \pi \left(\frac{5}{2} r_{\oplus}^3 + 4r_{\ominus}^3 \right)}{16\sqrt{2}r_{\ominus}^3}$$

23. (4) No. of X particles per unit cell = 4

No. of Y particles = 4

No. of Z particles = 8

Along one body diagonal 2X atoms from 2 corners, one Y particle and 2Z particles will be removed.

So, effective no. of X particles in a unit cell

$$= 4 - \frac{1}{8} \times 2 = \frac{15}{4}$$

Effective no. of Y particles in a unit cell

$$= 4 - 1 = 3$$

Effective no. of Z particles in a unit cell

$$= 8 - 2 = 6$$

$$X : Y : Z$$

$$\frac{15}{4} : 3 : 6$$

$$5 : 4 : 8$$

24. (1) Effective no. of A particles are removed

$$= 4 \times \frac{1}{8} + 2 \times \frac{1}{2} = \frac{3}{2}$$

Effective no. of A particles present in a unit cell

$$= 4 - \frac{3}{2} = \frac{5}{2}$$

Effective no. of B particles are removed

$$= 2 \times \frac{1}{4} + 1 = \frac{3}{2}$$

Effective no. of B particles present in a unit cell

$$= 4 - \frac{3}{2} = \frac{5}{2}$$

$$A : B$$

$$\frac{5}{2} : \frac{5}{2} \text{ or } 1 : 1$$

25. (2) Volume of hcp unit cell

$$= 24 \sqrt{2} r^3$$

$$(a = 2r = \frac{100}{\sqrt{2}} \text{ pm})$$

$$\therefore r = \frac{100}{2\sqrt{2}} \text{ pm.}$$

$$r^3 = \frac{10^6}{8 \times 2 \times \sqrt{2}}$$

$$\therefore V = \frac{24 \times \sqrt{2} \times 10^6}{8 \times 2 \times \sqrt{2}} = 1.5 \times 10^6$$

26. (2) A crystal possesses only centre of symmetry.
 27. (2) TiO_2 has tetragonal system with five planes of symmetry and five axes of symmetry.
 28. (1) $f + c = e + 2$; where f is plane, c is interfacial angle and e is straight edges.
 29. (2) Ice has hexagonal structure with $a = b \neq c$ & $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.
 30. (2) Ice has hexagonal structure with $a = b \neq c$ & $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$.
 31. (3) The plane is passing through 6 atoms present on two opposite face diagonals.

32. (2) In bcc $r = \frac{\sqrt{3}a}{4}$

Also, edge length of unit cell = a

Radius of atom = r

$\therefore$ edge length not covered by atom = $a - 2r$

$$a - \frac{\sqrt{3}}{2}a = a \left[\frac{2 - \sqrt{3}}{2} \right]$$

$\therefore$ Percentage fraction not covered

$$= \frac{a \left(\frac{2 - \sqrt{3}}{2} \right)}{a} \times 100 = 13.4 \times 100 = 13.4\%$$

33. (4) For fcc, number of X atoms = 4/unit cell
 Number of TVs = $8Z$
 Number of OVs = $4Y$
 Number of atoms removed along one body diagonal
 = $2X$ (corner) and $2Z$ (TVs) and $1Y$ (OV at body centre)

$$\therefore \text{Number of X atoms left} = 4 - \left(2 \times \frac{1}{8} \right) = \frac{15}{4}$$

$$\text{Number of Y atoms left} = 4 - (1 \times 1) = 3$$

$$\text{Number of Z atoms left} = 8 - (2 \times 1) = 6$$

$$\begin{aligned} \text{The simplest formula} &= \text{X}_{\frac{15}{4}} \text{Y}_3 \text{Z}_6 \Rightarrow \text{X}_{15} \text{Y}_{12} \text{Z}_{24} \\ &\Rightarrow \text{X}_5 \text{Y}_4 \text{Z}_8 \end{aligned}$$

34. (3) From figure, it is clear 4 corners and 2 face centres lie on the shaded plane. Therefore, there will be six C atoms, and atoms (marked A) in TVs do not touch other.

Fig. (1) is not possible; four atom marked C.

Fig. (2) is not possible, atoms A in TVs are not shown in figure.

Fig. (3) is possible, since atoms A in TVs are not touching each other.

Fig. (4) is not possible, since atoms A in TVs are touching each other.

35. (3) Refer to Section 1.22[c(iv)].

$$\begin{aligned} \text{Distance between two layer (A and B)} &= \frac{c}{2} = \sqrt{\frac{8}{3}} (r) \\ &= \sqrt{\frac{2}{3}} (2r) \end{aligned}$$

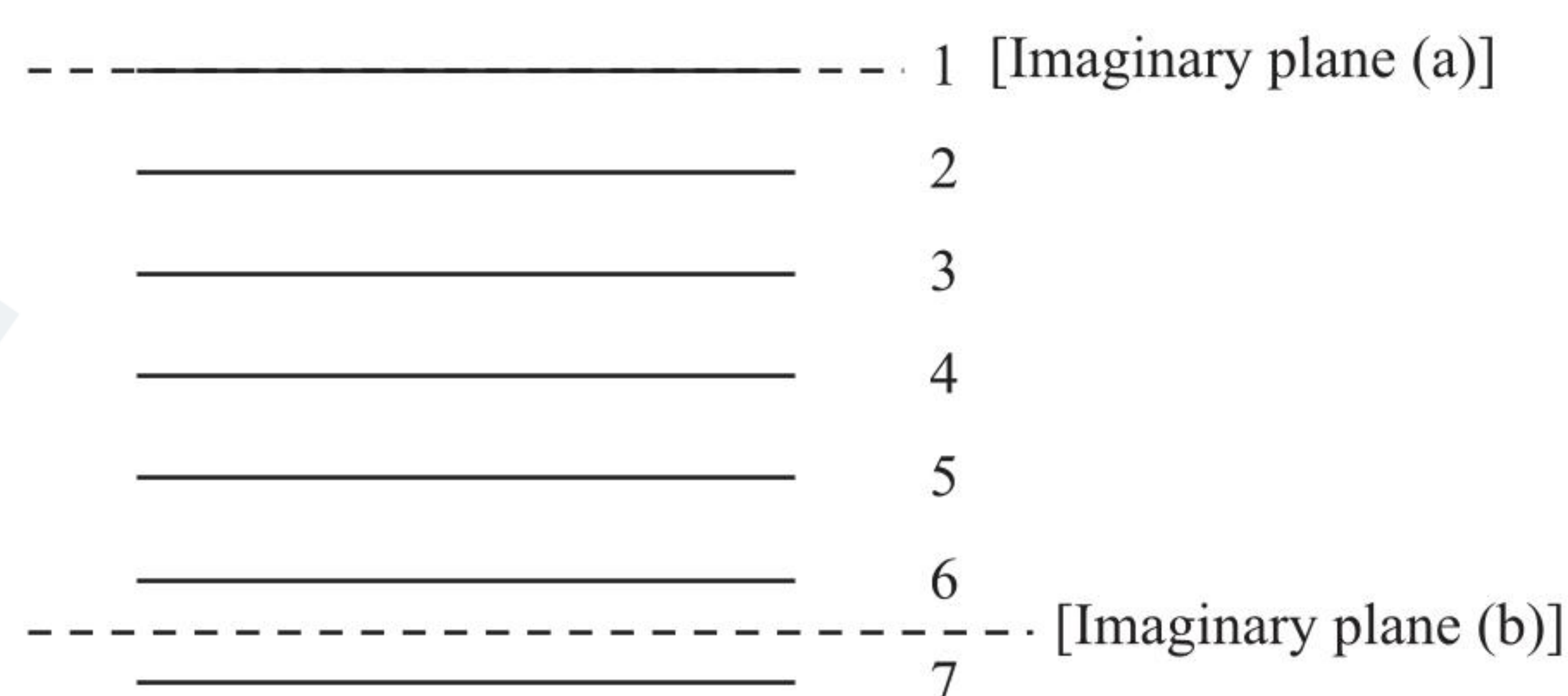
$$\left[\begin{array}{l} \text{Given distance between two imaginary} \\ \text{Plane} = 13 \frac{\sqrt{2}}{\sqrt{3}} (r) \end{array} \right]$$

Let K is the number of imaginary planes.

Hence,

$$K \times \frac{\sqrt{2}}{\sqrt{3}} (2r) = 13 \frac{\sqrt{2}}{\sqrt{3}} (r) \Rightarrow K = \frac{13}{2} = 6.5 \approx 7$$

Thus, maximum number of layers = 7 (see figure below).



36. (4) $\text{Ni} = 3d^8 4s^2$ (At. no. = 28),
 $\therefore \text{Ni}^{2+} = 3d^8$ and $\text{Ni}^{3+} = 3d^7$
 Hence, 96% ion of Ni^{2+} and 4% ions of Ni^{3+} are present.
 Let number of O^{2-} ion present in the crystal = x .

Applying electroneutrality rule,

Total positive charge = Total negative charge

$$96 \times 2 (+\text{ve charge}) + 4 \times 3 (+\text{ve charge}) = x \times 2 (-\text{ve charge})$$

$$\therefore 96 \times 2 + 4 \times 3 - 2x = 0$$

$$\therefore x = 1.02$$

So formula of crystal $\text{Ni}_{1.00} \text{O}_{1.02}$ or $\text{Ni}_{0.98} \text{O}_{1.00}$.

37. (4) Density (ρ) = $\frac{Z_{\text{eff}} \times M_w}{N_A \times a^3}$
 (For antifluorite, $Z_{\text{eff}} = 4/\text{unit cell}$)

$$\begin{aligned} \rho &= \frac{4 \times [23 \times 2 + 16]}{6 \times 10^{23} \times (100 \text{ pm} \times 10^{-10} \text{ cm})^3} \left[\begin{array}{l} 1 \text{ pm} = 10^{-12} \text{ m} \\ = 10^{-10} \text{ cm} \end{array} \right] \\ &= 414.16 \text{ g cm}^{-3} \end{aligned}$$

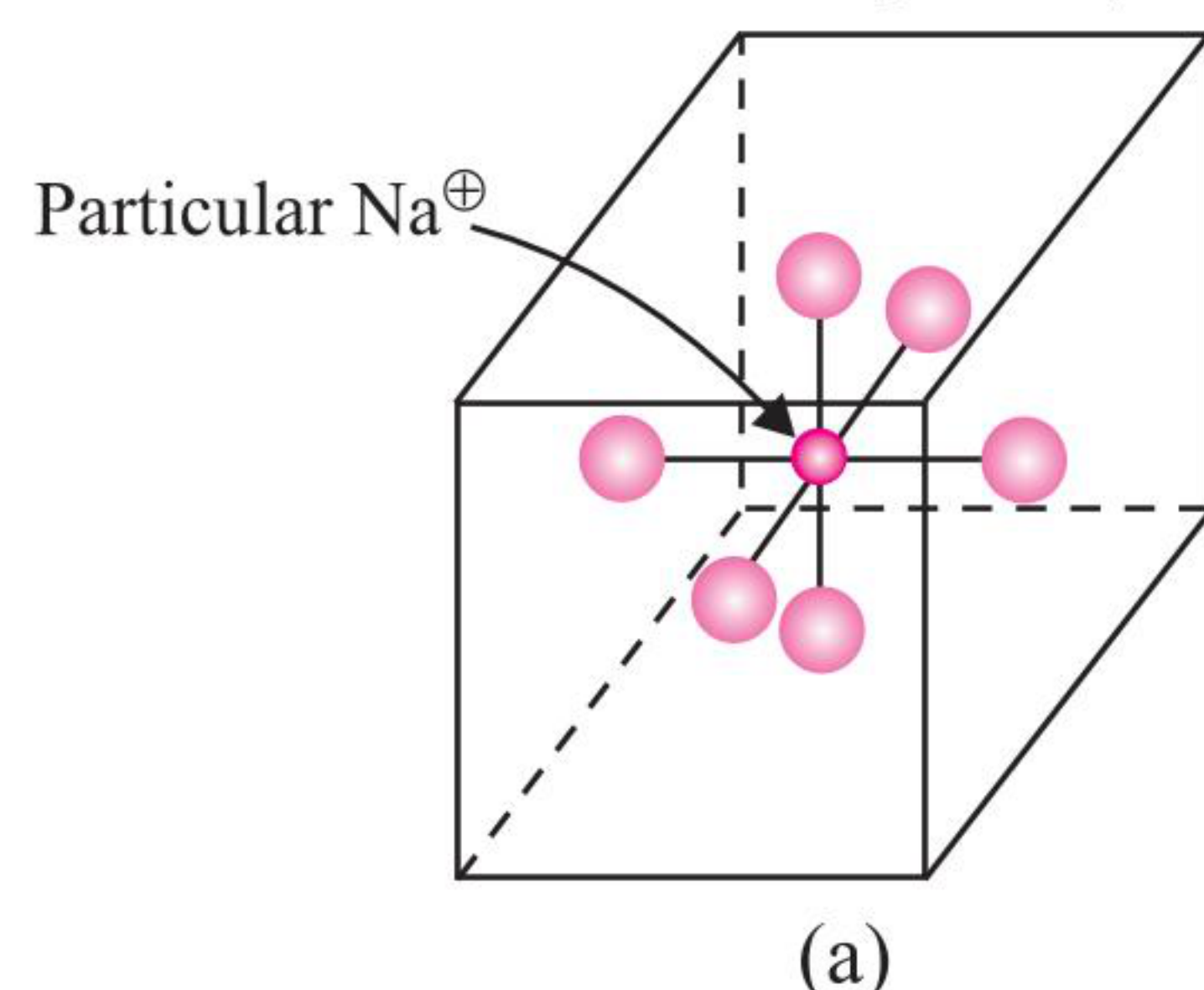
Note: Frenkel defect does not change the density of the crystal.

38. (2) In fluorite-type structure, CN = 8 : 4 (factual statement).
 39. (2) ABAB type of packing means ccp packing in which 74% space is occupied and 26% is empty.

40. (3) In fcc structure, corner atoms do not touch each other (atoms 1 and 2), but every face centre atom touches corners. Moreover, every face centre atom touches every other face centre atom provided it is not the opposite face centre atom in an fcc unit cell.

- Atoms 3 and 4 are touching each other where centre-to-centre distance = $\frac{a}{\sqrt{2}}$
- Atoms 1 and 2 are not touching each other.
- Atoms 2 and 4 are touching each other where centre-to-centre distance = $\frac{a}{\sqrt{2}}$

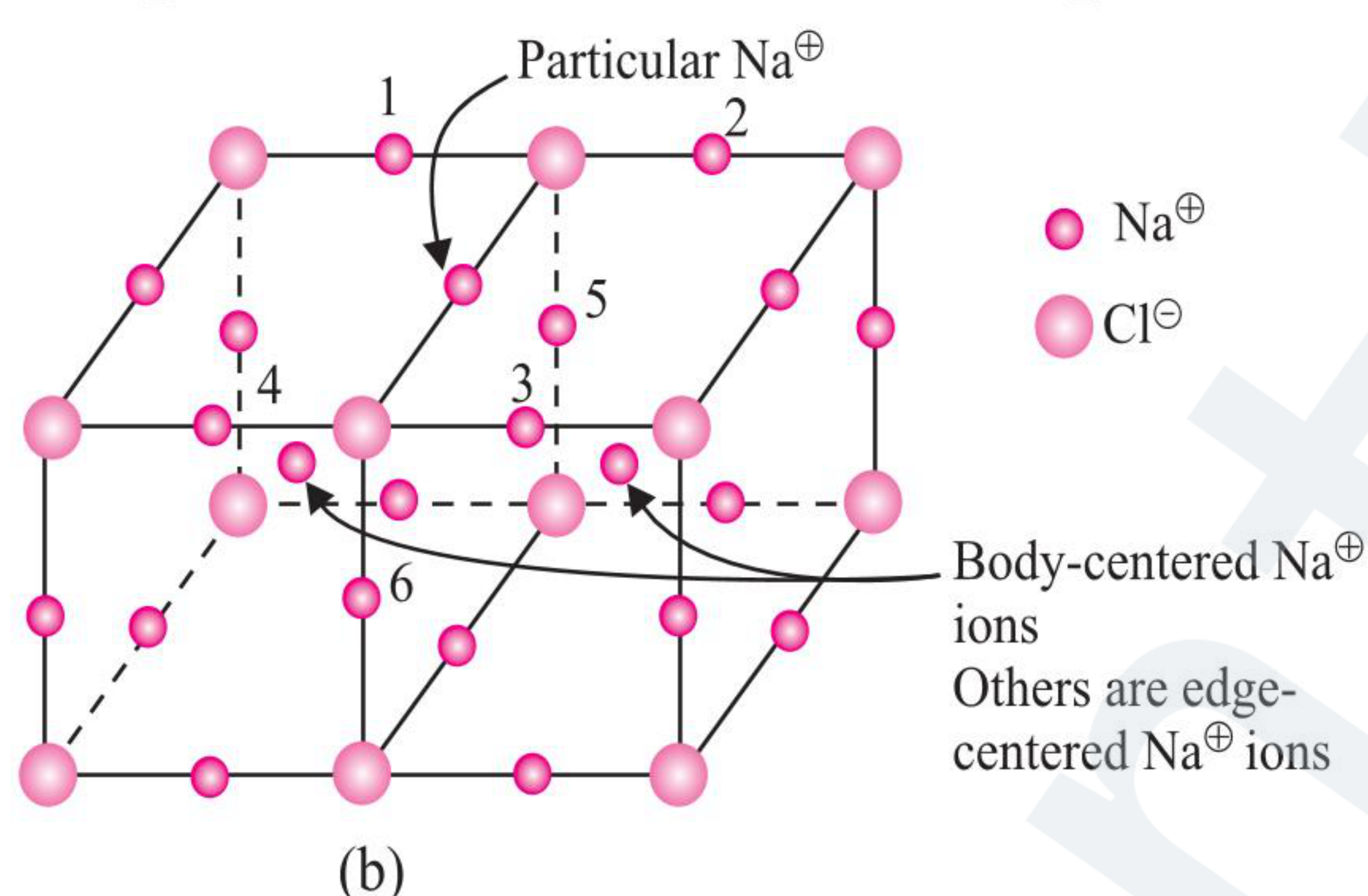
41. (2) $\text{Na}^{\oplus}$ lies in OV's formed by $\text{Cl}^{\ominus}$ ($\text{Na}^{\oplus}$ touches six $\text{Cl}^{\ominus}$ ions)



$\text{Na}^{\oplus}$ and $\text{Cl}^{\ominus}$ are not shown touching in the figure.

Each atom shown is present at the face centre of each cube.

$$\left[\text{Distance between } \text{Na}^{\oplus} \text{ and } \text{Cl}^{\ominus} = \frac{a}{2} \right]$$



Try to visualize two cubes exactly above these two cubes.

Each atom shown is present at the edge centre and body centre of each cube.

$$\text{Distance between two nearest } \text{Na}^{\oplus} = \frac{a}{\sqrt{2}}$$

- Thus, the number of nearest neighbours of $\text{Na}^{\oplus}$ ion = 6 $\text{Cl}^{\ominus}$ ions
- The number of next nearest neighbours of $\text{Na}^{\oplus}$ ion = 12 $\text{Na}^{\oplus}$ ions

Note: Next nearest neighbours are shown by number 1, 2, 3, ... 6 in Fig. (b). Likewise 6 next nearest neighbours of $\text{Na}^{\oplus}$ ions will be in the above two cubes. Hence, total number of next nearest neighbours of $\text{Na}^{\oplus}$ ions = 12 $\text{Na}^{\oplus}$ ions.

42. (1) It is clear from the figure that the arrangement is sc, with coordination number (CN) of each point = 6.

(The arrangement shown in figure consists of 4 unit cells. Taking a view of one unit cell, the atoms are not present at the face centres of each unit cell, hence it cannot be fcc, since in fcc lattice points are occupied at corners and face centres of each unit cell).

$$43. (1) \rho = \frac{Z_{\text{eff}} \times M_w}{a^3 \times 10^{-30} \times N_A} \quad [\text{For fcc, } Z_{\text{eff}} = 4/\text{unit cell}]$$

$$\begin{aligned} \therefore M_w &= \frac{\rho \times a^3 \times 10^{-30} \times N_A}{Z_{\text{eff}}} \\ &= \frac{\left(10.0 \text{ g cm}^{-3} \times (200 \text{ pm})^3 \times 10^{-30} \text{ cm}^3 \right)}{\left(\times 6 \times 10^{23} \text{ atoms} \right)} \\ &= 12 \text{ g mol}^{-1} \end{aligned}$$

Thus, 12 g mol⁻¹ contains = N_A atoms = 6×10^{23} atoms

$$\therefore 100 \text{ g contains} = \frac{6 \times 10^{23}}{12} \times 100 = 5 \times 10^{24} \text{ atoms}$$

44. (2)

45. (1) Si has fcc structure ($Z_{\text{eff}} = 4$ and Si is also present in alternate TVs (= 4). So the total number of atoms = 4 + 4 = 8/unit cell.

Note: Si has diamond cubic structure, refer Section 1.17.

$$\begin{aligned} \therefore \rho &= \frac{Z_{\text{eff}} \times A_w}{N_A \times a^3} \quad \left[\text{Mass of Si atom} = \frac{A_w}{N_A} \right] \\ &= \frac{8 \times \text{Mass of Si atom}}{a^3} \\ &= \frac{8 \times (28.08 \times 1.66 \times 10^{-27}) \text{ kg}}{(5.43 \times 10^{-10})^3 \text{ m}^3} \quad [1 \text{ \AA} = 10^{-10} \text{ m}] \\ &= 2330 \text{ kg m}^{-3}. \end{aligned}$$

$$46. (2) \frac{r_{\oplus}}{r_{\ominus}} \left(\text{i.e., } \frac{r_{\text{Ga}^{\oplus}}}{r_{\text{As}^{3-}}} \right) = \frac{1.22 \text{ \AA}}{1.25 \text{ \AA}} = 0.976$$

From radius ratio, it is clear that cation (Ga^{3+} ion) lies in body centred or cubic void, where

$$\begin{aligned} 2(r_{\oplus} + r_{\ominus}) &= \sqrt{3}a \\ 2(1.22 + 1.25) \text{ \AA} &= \sqrt{3}a \Rightarrow a = 2.852 \end{aligned}$$

$$47. (2) \frac{r_{\oplus}}{r_{\ominus}} \left(\text{i.e., } \frac{r_{\text{Zn}^{\oplus}}}{r_{\text{S}^{2-}}} \right) = \frac{0.74 \text{ \AA}}{1.70 \text{ \AA}} = 0.44$$

From radius ratio, it is expected that Zn^{2+} ion occupy OV's; however, the value of 0.44 is only slightly larger than $r_{\text{void}}/r_{\ominus} = 0.414$ for OV. There is also some covalent character in the $\text{Zn}^{2+}\text{-S}^{2-}$ interaction, which tends to shorten the interatom distance.

Note: Experimentally, it was found that Zn^{2+} ions occupy TVs.

$$\begin{aligned} \therefore (r_{\text{Zn}^{2+}} + r_{\text{S}^{2-}}) &= \frac{\sqrt{3}}{4}a \\ (0.74 + 1.70) \text{ \AA} &= \frac{\sqrt{3}}{4}a \Rightarrow a = 5.634 \text{ \AA} \end{aligned}$$

48. (2) For bcc, $Z_{\text{eff}} = 2/\text{unit cell}$
For fcc, $Z_{\text{eff}} = 4/\text{unit cell}$

$$\therefore \text{Ratio} = \frac{2}{4} = 0.5$$

49. (2) For bcc,

$$(r_{\oplus} + r_{\ominus}) = \frac{\sqrt{3}}{2}a$$

$$338 \text{ pm} = \frac{\sqrt{3}}{2}a \Rightarrow a = 390.3 \text{ pm}$$

50. (1) For fcc,

$$(r_{\oplus} + r_{\ominus}) = \frac{a}{2}$$

$$r_{\oplus} + 144 \text{ pm} = \frac{508 \text{ pm}}{2}$$

$$\therefore r_{\oplus} = 110 \text{ pm}$$

51. (1) Z_{eff} for fcc = 4 and for bcc = 2/unit cell

$$\frac{\rho_{\gamma}}{\rho_{\beta}} = \frac{\rho_{\text{fcc}}}{\rho_{\text{bcc}}} = \frac{Z_{\text{eff(fcc)}}}{Z_{\text{eff(bcc)}}} \times \left(\frac{a_{\text{bcc}}}{a_{\text{fcc}}} \right)^3$$

$$= \frac{4}{2} \times \left(\frac{290}{386} \right)^3 = 0.9788$$

52. (1) $\rho = \frac{Z_{\text{eff}} \times Mw}{a^3 \times N_A}$

$$2.165 \text{ kg m}^{-3} = \frac{Z_{\text{eff}} \times 58.5 \times 10^{-3} \text{ kg mol}^{-1}}{(562 \times 10^{-12})^3 \text{ m}^3 \times 6 \times 10^{23} \text{ atoms}}$$

$\therefore Z_{\text{eff}} = 4$ (fcc-type structure).

$\therefore$ For fcc,

$$d_{\text{A}^{\oplus}\text{B}^{\ominus}} = \frac{a}{2} = \frac{562}{2} = 281 \text{ pm}$$

53. (2) $\rho = \frac{Z_{\text{eff}} \times Mw}{a^3 \times N_A}$

$$1.74 \text{ g cm}^{-3} = \frac{Z_{\text{eff}} \times 24}{(4.53 \times 10^{-8})^3 \text{ cm}^3 \times 6 \times 10^{23} \text{ atoms}}$$

$\therefore Z_{\text{eff}} = 4$ (fcc structure)

For fcc, the radius of atom is:

$$r = \frac{a}{2\sqrt{2}} = \frac{4.53 \text{ Å}}{2\sqrt{2}} = 1.60 \text{ Å} = 160 \text{ pm}$$

54. (1) Packing fraction ion fcc, bcc, and sc are 0.74, 0.68, and 0.52, respectively.

$$\therefore \text{Ratio} = \frac{0.74}{0.74} : \frac{0.68}{0.74} : \frac{0.52}{0.74}$$

$$= 1 : 0.92 : 0.70$$

55. (3) For fcc, $Z_{\text{eff}} = 4$ /unit cell

Mw of NaCl = 58.5 g mol^{-1}

$$\text{Number of atoms in 1.0 g NaCl} = \frac{6 \times 10^{23}}{58.5}$$

$$\text{Number of unit cells in 1.0 g NaCl} = \frac{6 \times 10^{23}}{58.5 \times 4} = 2.57 \times 10^{21} \text{ unit cells}$$

56. (4) For fcc, $Z_{\text{eff}} = 4$ /unit cell

$$\text{Volume of atoms in the unit cell} = \frac{4}{3} \pi r^3 \times Z_{\text{eff}}$$

$$= \frac{4}{3} \pi r^3 \times 4$$

$$= \frac{16}{3} \pi r^3$$

57. (2) Let the volume of unit cell = V

Volume occupied by atoms = $0.68V$

Thus,

$$Z_{\text{eff}} \left(\frac{4}{3} \pi r^3 \right) = 0.68V$$

Also, $2r = 2.86 \text{ Å} \Rightarrow r = 1.43 \text{ Å}$

$$\rho = \frac{Z_{\text{eff}} \times Aw}{a^3 \times N_A} \quad \left(\frac{Aw}{N_A} = \text{mass of an atom in amu} \right)$$

Applying another formula of ρ .

(Refer Section 1.13, alternative method)

$$\rho = \frac{Z_{\text{eff}} \times \text{Mass in amu} \times 1.66 \times 10^{-27} \text{ kg}}{V}$$

$$8570 \text{ kg m}^{-3} = \frac{0.68 \times m \times 1.66 \times 10^{-27} \text{ kg}}{\frac{4}{3} \pi (1.43)^3 \times 10^{-30}}$$

$\therefore m \Rightarrow 93 \text{ amu}$

58. (2) (Refer Section 1.13, alternative method)

$$\rho = \frac{\left[\sum (\text{Number of atom of each kind}) \times (Mw \text{ of each kind}) \times 1.66 \times 10^{-27} \text{ kg} \right]}{a^3}$$

$$7717 \text{ kg m}^{-3} = \frac{\left[(\text{Number of Sn atoms}) \times (118.7 \times 1.66 \times 10^{-27}) + (\text{Number of Cu atoms}) \times (63.54 \times 1.66 \times 10^{-27}) \right]}{(3.903 \times 10^{-10})^3 \text{ m}^3}$$

$$276.4 = n_{\text{Sn}}(118.7) + n_{\text{Cu}}(63.54)$$

$$4.35 = 1.86n_{\text{Sn}} + n_{\text{Cu}}$$

$$n_{\text{Cu}} = 4 \Rightarrow n_{\text{Sn}} = 0.188$$

$$\text{Atomic fraction} = \frac{n_{\text{Sn}}}{n_{\text{Sn}} + n_{\text{Cu}}} = 0.05$$

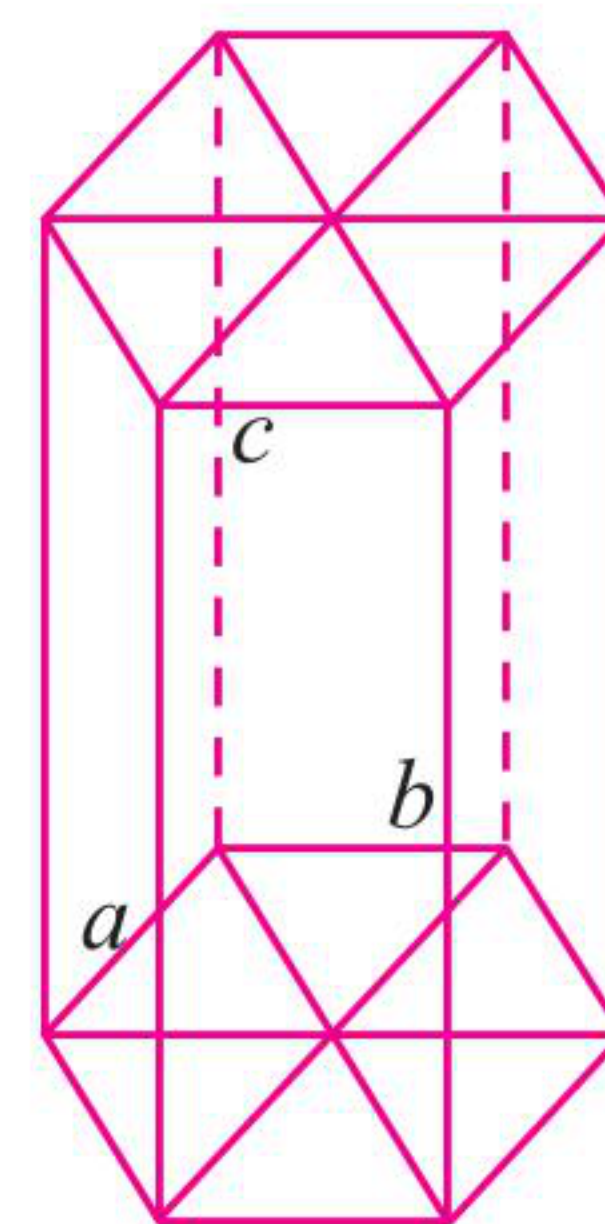
59. (3) The volume available = $\frac{0.015}{7.5 \times 10^3}$

$$(\text{Number of unit cells}) \times (400 \times 10^{-12})^3 = \frac{0.015}{7.5 \times 10^3}$$

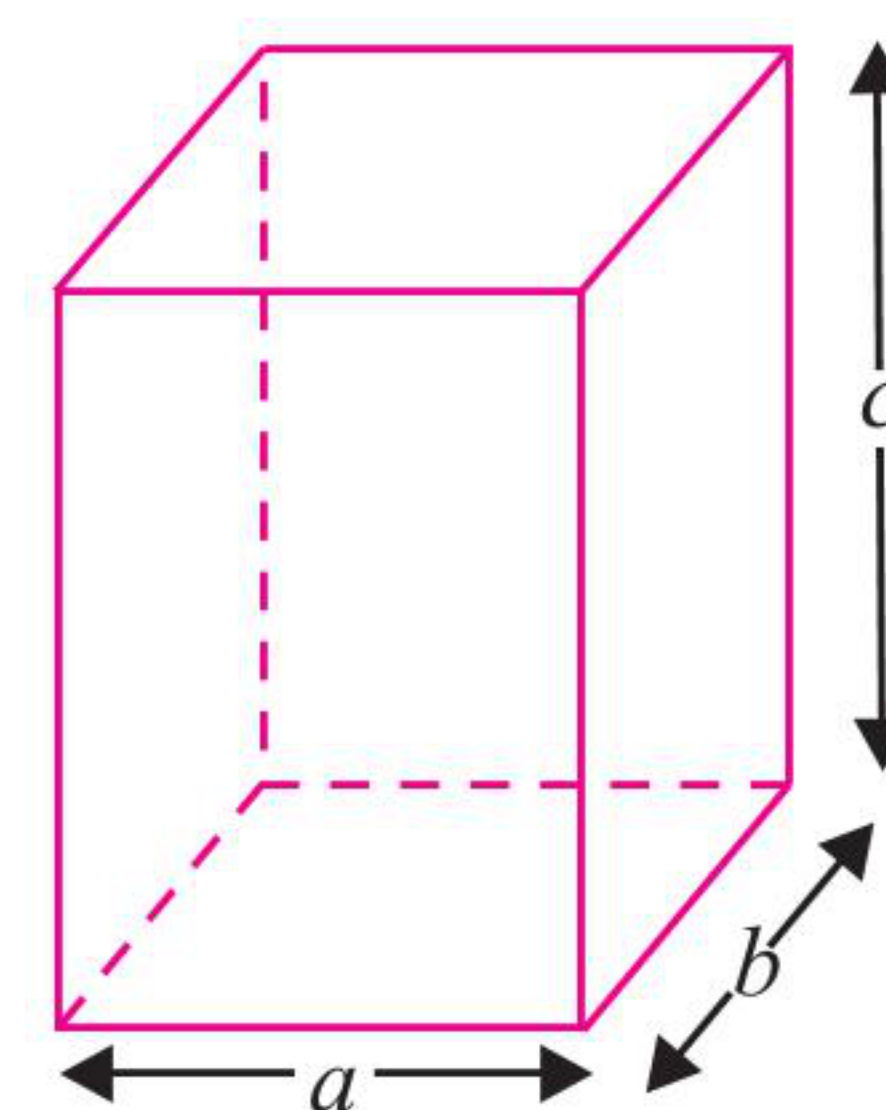
$$\Rightarrow \text{Number of unit cell} = 3.125 \times 10^{22}$$

60. (2) Ratio = $\frac{abc}{6 \times \left(\frac{\sqrt{3}}{4} a^2 \right) \times c} = \frac{2}{3\sqrt{3}}$

Note: $\frac{c}{a} = \frac{2\sqrt{2}}{\sqrt{3}}$ for an ideal hcp [Refer Section 1.22(f and g)].



Hexagonal unit cell



Tetragonal unit cell

61. (4) Number of atoms = N_A

$$\Rightarrow \text{Number of unit cells} = \frac{N_A}{4}$$

[$\because$ 4 atoms in each unit cell]

$$\begin{aligned}\text{Volume of 1 mol lattice} &= \frac{N_A}{4} \times \text{Volume of unit cell} \\ &= \frac{6.023 \times 10^{23}}{4} \times (400 \times 10^{-12})^3 \text{ m}^3 = 9.64 \text{ mL}\end{aligned}$$

62. (2) For bcc, $r = \frac{\sqrt{3}}{4} a$

Edge length not covered by atom = $a - 2r$

$$= a - 2 \times \frac{\sqrt{3}}{4} a$$

$$= a \left[\frac{2 - \sqrt{3}}{2} \right]$$

$$\begin{aligned}\therefore \% \text{ of fraction not covered} &= \frac{a \left[\frac{2 - \sqrt{3}}{2} \right]}{a} \times 100 \\ &= 0.134 \times 100 = 13.4\%\end{aligned}$$

63. (1) i. Edge length = $AB = AD = BC = CD = a$

ii. $AC = \sqrt{(AB^2) + (BC^2)} = \sqrt{a^2 + a^2} = \sqrt{2} a$

iii. $AG = \sqrt{(AC^2) + (CG^2)} = \sqrt{2a^2 + a^2} = \sqrt{3} a$

64. (1) i. Edge length = $AB = AD = BC = CD = a$

ii. $AC = \sqrt{2} a$

iii. AG (body diagonal) = $\sqrt{3} a$

Therefore $AA' = AG/2 = \frac{\sqrt{3}}{2} a$

65. (3) $\frac{r_{A^+}}{r_{B^-}} = 0.50$ and $\frac{r_{C^+}}{r_{B^-}} = 0.70$

$$\Rightarrow \frac{r_{A^+} + r_{B^+}}{r_{B^-}} = 1 + 0.5 = 1.5$$

Similarly, $\frac{r_{C^+} + r_{B^-}}{r_{B^-}} = 1.70$

$$\therefore \frac{r_{A^+} + r_{B^-}}{r_{C^+} + r_{B^-}} = \frac{1.5}{1.7} = 0.88$$

Also, $a_{AB} = 2(r_{A^+} + r_{B^-})$ and $a_{CB} = 2(r_{C^+} + r_{B^-})$

$$\therefore \frac{a_{AB}}{a_{CB}} = \frac{1.5}{1.7} = 0.88$$

66. (2) Volume of unit cell = $a \times b \times c = 5 \times 10^{-8} \times 8 \times 10^{-8} \times 4 \times 10^{-8}$
 $= 1.6 \times 10^{-22} \text{ cm}^3$

Mass of unit cell = $1.6 \times 10^{-22} \times 5.2 = 8.32 \times 10^{-22} \text{ g}$

Number of molecules in one unit cell = $\frac{8.32 \times 10^{-22} \text{ g}}{166.4 \text{ g mol}^{-1}} = 3$

67. (4) Number of unit cell for bcc is 2 and fcc is 4.

68. (2) W atoms/unit cell = $8 \times \frac{1}{8} = 1$

O atoms/unit cell = $12 \times \frac{1}{4} = 3$

Na atoms/unit cell = 1

Hence, formula is NaWO_3 .

69. (2) CN of (8: 8) of Li^+ and Ag^+ suggest bcc structure.

70. (1) For face-centred cubic unit cell (e.g., that of NaCl), edge length = $2 \times \text{Distance between cation and anion} = 2(r_c + r_a) = 508 \text{ pm}$ (given). Putting $r_c = 110 \text{ pm}$, we get $r_a = 144 \text{ pm}$.

71. (3) Cs^+ and I^- ions have largest sizes.

72. (4)

73. (2)

74. (1) Number of A atoms = $8 \times \frac{1}{8} = 1$
 Number of B atoms = $6 \times \frac{1}{2} = 3$ } Formula = AB_3 .

75. (3) $58.5 \text{ g NaCl} = 1 \text{ mol}$
 $= 6.02 \times 10^{23} \text{ Na}^+\text{Cl}^- \text{ units}$

One unit cell contains 4 Na^+Cl^- units. Hence, number of the unit cell present = $6.02 \times 10^{23}/4 = 1.5 \times 10^{23}$

76. (3)

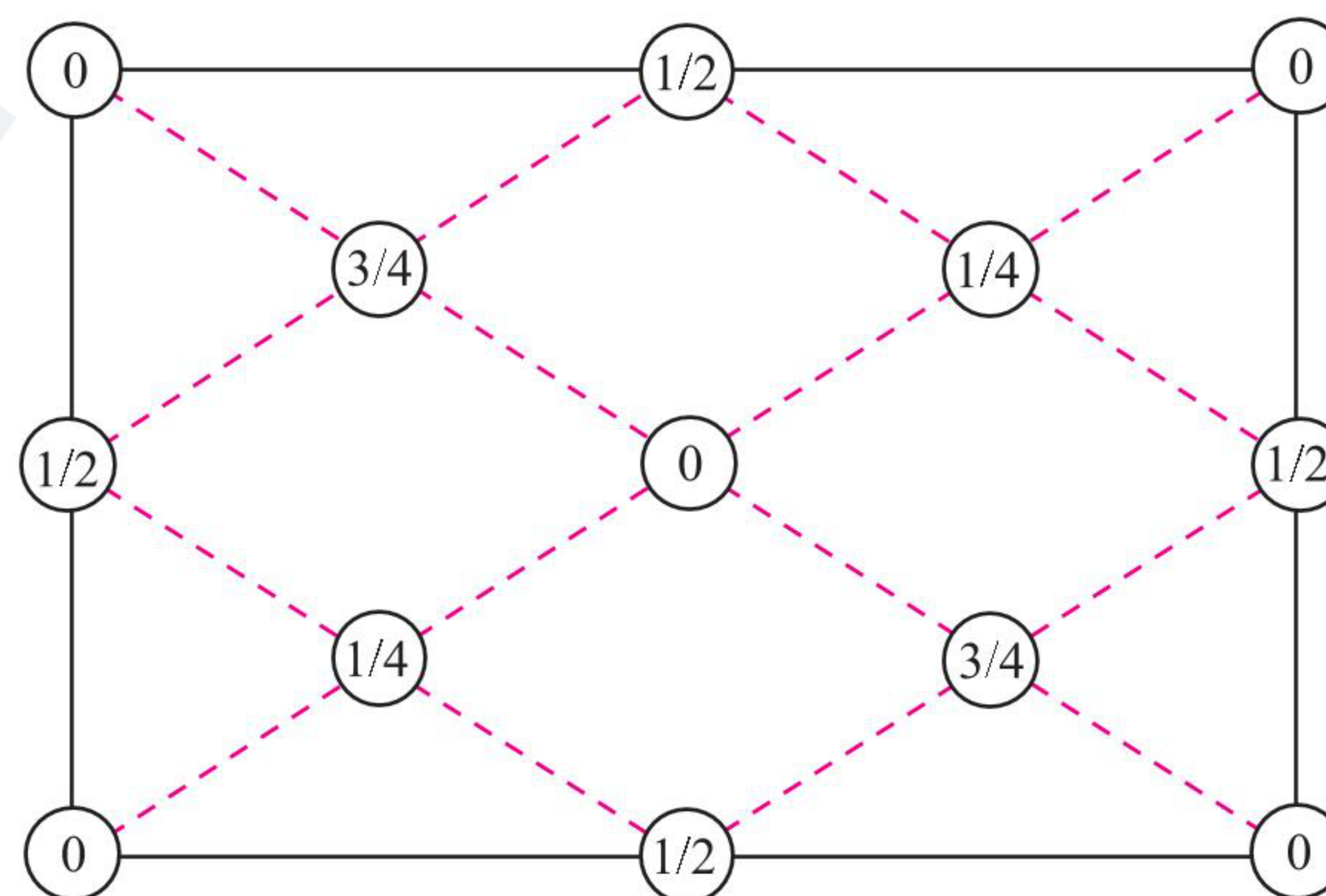
77. (3)

78. (3)

79. (4) hcp has 12 nearest neighbours.

80. (3) As CsCl is body-centred, $d = \sqrt{3}a/2$.

81. (1) The space lattice of diamond is fcc. The primitive basis has two identical atoms at $0, 0, 0$ and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ associated with each point of the fcc lattice as shown in the figure.



82. (2) ZnS has diamond cubic structure in which S^{2-} ions form fcc lattice and Zn^{2+} ions are present in alternate TVs.

Z_{eff} of $\text{S}^{2-} = 4$ (corner + face centre = $1 + 3 = 4$).

Z_{eff} of $\text{Zn}^{2+} = 4$

(Total TVs = 8, alternative TVs = 4).

So Z_{eff} of ZnS = 4.

Hence, the formula is Zn_4S_4 .

So coordination number of Zn^{2+} and S^{2-} is 4 each.

83. (4) $r = \frac{\sqrt{3}}{4} a$ [Refer Section 1.10 (b)].

84. (2) $r_{\oplus} + r_{\ominus} = a/2$ (Refer Section 1.16.4).

85. (4) Since Si atom forms fcc arrangement, i.e., Si atoms are present at the corner and face centre.

$\therefore Z_{\text{eff}}$ for Si atom for fcc arrangement = 4 atom/unit cell

Number of TVs = 8 atoms/unit cell

Number of Si atoms occupying TVs = 4

$\therefore$ Total number of Z_{eff} for Si atoms

$$= \left(\frac{1}{8} \times 8 \right) + \left(\frac{1}{2} \times 6 \right) + (1 \times 4)$$

= 8 atoms/unit cell.

86. (4) Orthorhombic (refer Table 1.3).

87. (2) Number of A atoms at alternate corners

$$= 4 \text{ corner} \times \frac{1}{8} \text{ per corner share} = \frac{1}{2}$$

Number of B atoms at alternate face

$$= 2 \text{ faces} \times \frac{1}{2} \text{ per face center share} = 1$$

Number of C atoms at alternate edges and at body centre

$$= \left(4 \text{ edges} \times \frac{1}{4} \text{ per edge centre share} \right) + 1 \text{ atom at body centre}$$

$$= 1 + 1 = 2$$

Thus, formula: $A_1 B_1 C_2$

Simplifying, AB_2C_4 .

88. (4) For bcc structure of an ionic compound, CN of cation = CN of anion = 8. [Refer Section (1.16.2)]

$$89. (2) \rho = \frac{Z_{\text{eff}} \times Aw \text{ of Al}}{N_A \times a^3}, Z_{\text{eff}} = ?$$

$$2.72 \text{ g cm}^{-3} = \frac{Z_{\text{eff}} \times 27}{6.023 \times 10^{23} \times (404 \times 10^{-10})^3}$$

$$\therefore Z_{\text{eff}} \approx 4$$

Hence, it forms fcc structure with CN = 12.

90. (4) In fluorite-type structure, CN = (8 : 4) (cation : anion) (Th^{4+} : O^{2-})

$$\text{Formula} = 4\text{ThO}_2 = \text{Th}_4\text{O}_8 (Z_{\text{eff}} = 4)$$

Note: Bivalent ion is O^{2-} .

CN of cation = Number of effective anion = 8 (O^{2-})

CN of anion = Number of effective cation = 4 (Th^{4+})

Note: Since it is fluorite-type structure, here O^{2-} occupies all 8 TVs and Th^{4+} in ccp or fcc arrangement.

91. (2) CN of Th^{4+} = 8 (as explained in Q.90 above).

92. (1) Since CsBr is bcc type, so CN = 8 : 8 (cation : anion).

93. (2) Packing factor in sc = $\pi/6$.

$$94. (1) \text{ For fcc type, } r = \frac{a}{2\sqrt{2}} = \frac{620 \text{ pm}}{2 \times 1.414} = 219.20 \text{ pm}$$

95. (3) In ZnS-type structure, anions form fcc and cations are present in alternate TVs.

In BeO, Number of O^{2-} = Corner + Face centre

$$= 1 + 3 = 4$$

Number of Be^{2+} = 4 (alternate TVs)

Number of Mg^{2+} introduced = 4 (available TV = 4)

So CN of Be^{2+} and Mg^{2+} ions = 4 : 4

96. (2) i. Number of O^{2-} = 4

Number of Be^{2+} = 4

Number of Mg^{2+} = 4

ii. Be^{2+} and Mg^{2+} are present in TVs and they are present on each body diagonal of the cube.

When single body diagonal is removed,

Number of corner ions (O^{2-}) removed

$$= 2 \times \frac{1}{8} \text{ per corner share} = \frac{1}{4} = 0.25$$

$$\text{Number of } \text{O}^{2-} \text{ left} = 4 - 0.25 = 3.75$$

iii. Number of Be^{2+} removed = 1

$$\text{Number of } \text{Be}^{2+} \text{ left} = 4 - 1 = 3$$

iv. Number of Mg^{2+} removed = 1

$$\text{Number of } \text{Mg}^{2+} \text{ left} = 3$$

Thus, formula is: $\text{Mg}_3\text{Be}_3\text{O}_{3.75}$.

97. (3) Refer Section 1.18.

98. (2) An octahedral holes is formed by 6 sphere.

99. (2) No. of nearest neighbour = 8 (All body centre atom w.r.t corner atom)

No. of next nearest neighbour = 6 (No. of corner atom along edge w.r.t any corner)

100. (3) In diamond C-atoms are present in fcc lattice points as well as in alternate tetrahedral void.

101. (1)

$$102. (2) \frac{\sqrt{3}a}{4} = (2R), \quad \frac{\sqrt{3} \times 356}{4} = 1.732 \times 89 = 154.14$$

$$\therefore 2R = 154.14$$

103. (4) Octahedral void present at the centre of cube and tetrahedral void is present at $(1/4)^{\text{th}}$ of the distance along each body diagonal.

$$\therefore \frac{\sqrt{3}a}{2} = 2 \times \text{distance between octahedral and tetrahedral void.}$$

104. (2) Z_{eff} of NaCl (rock salt) = 4. Formula : A_4B_4

All 4 OV's are occupied. All 8 T.V's are empty.

$$\therefore \text{No. of C atoms} = 8$$

$$\therefore \text{Formula} = \text{A}_4\text{B}_4\text{C}_8 = \text{ABC}_2$$

105. (2) It is a fact. Four out of 8 tetrahedral voids are occupied by carbon

106. (3) In hcp, there is 6 atoms per unit cell.

$$\therefore \text{Number of octahedral voids} = 6$$

$$\therefore \text{Number of tetrahedral voids} = 2 \times 6 = 12$$

$$\therefore \text{Total number of voids per atom} = \frac{18}{6} = 3$$

$\therefore$ In 1 mole compound, the total no. of voids

$$= 3 \times 6.023 \times 10^{23}$$

$\therefore$ In 0.5 mole compound the total no. of voids

$$= 3 \times 0.5 \times 6.023 \times 10^{23} = 9.034 \times 10^{23}.$$

107. (3) This leads to stronger coulombic forces of attraction in NaF.

108. (4) NaCl posses rock-salt type structure with formula AB. ZnS posses Sphalerite type structure with formula AB.

109. (2) Let $x \text{ Cu}^{2+}$ and $(1.8 - x) \text{ Cu}^{\oplus}$ ions are present in the compound $\text{Cu}_{1.8}\text{S}$. Compound is electrically neutral.

$$\therefore +2x + (1.8 - x) - 2 = x = 0.2$$

$$\% \text{Cu}^{2+} = \frac{0.2}{1.8} \times 100 = 11.11$$

110. (2) For a given radius of anion ($r_{\ominus}$)

Radius ratio for OV and TV is as follows:

$$\left(\frac{r_{\oplus}}{r_{\ominus}} \right)_{\text{OV}} > \left(\frac{r_{\oplus}}{r_{\ominus}} \right)_{\text{TV}}$$

$$\left(\begin{array}{l} \text{For OV, } \frac{r_{\oplus}}{r_{\ominus}} = 0.414 - 0.732 \\ \text{For TV, } \frac{r_{\oplus}}{r_{\ominus}} = 0.225 - 0.414 \end{array} \right)$$

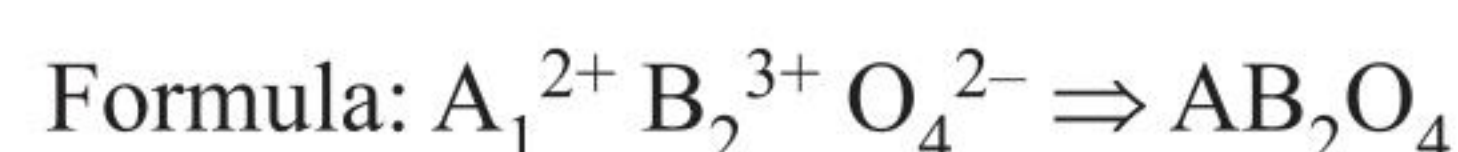
Hence, size of OV is larger than that of TV.

111. (4) For close-packed structure (fcc type)

Number of $\text{O}^{2-} = 4/\text{unit cell}$

$$\text{Number of } \text{A}^{2+} = \frac{1}{8} \times \text{TV} = \frac{1}{8} \times 8 = 1$$

$$\text{Number of } \text{B}^{3+} = \frac{1}{2} \times \text{OV} = \frac{1}{2} \times 4 = 2$$



112. (1) For OV,

$$\frac{R}{r} \left(\text{i.e., } \frac{r_{\oplus}}{r_{\ominus}} \text{ or } \frac{r_{\text{void}}}{r_{\ominus}} \right) = 0.414$$

$$\therefore \frac{r}{R} = \frac{1}{0.414} = 2.41$$

113. (1) Look at corner atom of fcc unit cell. A corner atom can support 8 unit cell. In each cube, at a distance of $\sqrt{3}a/4$ from corner atom, there is a tetrahedral void; it implies each atom is surrounded by eight tetrahedral voids. At the centre of edge, there is an octahedral void. Each corner can support six edges and hence it is surrounded by six octahedral voids.

114. (3) The next nearest neighbours to $\text{Cs}^{\oplus}$ are $\text{Cs}^{\oplus}$ of neighbour unit which are 6 in number.

115. (2) A TV in fcc is formed by 3 face centre atoms and one corner atom. In total, 8 such tetrahedrons are possible.

116. (4) Number of octahedral sites = Number of ions in the packing.

$$\therefore \text{Number of octahedral sites per sphere} = 1$$

117. (1) See text.

118. (3) Al_2O_3 is a corundum-type structure [refer Section 1.19]

In Al_2O_3 , anion (O^{2-}) forms fcc arrangement.

$$\therefore \text{Number of } \text{O}^{2-} = 4 \text{ (corner + face centre} = 1 + 3 = 4)$$

$$\therefore \text{Number of OVs} = 4.$$

$$\text{Cations } (\text{Al}^{3+}) \text{ are present} = \frac{2}{3} \times \text{OVs} = \frac{2}{3} \times 4 = \frac{8}{3}$$

$$\text{Hence, fraction of OVs filled by } \text{Al}^{3+} \text{ ion} = \frac{\frac{8}{3} \times 4}{4}$$

$$= 0.667$$

119. (2) In closest packing of atoms (e.g., fcc or ccp), there are 4 atoms at lattice point and 8 TVs/unit cell.

$$\text{or } \frac{8}{4} = 2 \text{ TVs/atom}$$

Similarly, there are 4 OVs/unit cell

$$\text{or } \frac{4}{4} = 1 \text{ OV/atom}$$

120. (3) $\text{Br}^{\ominus}$ in closest packed structure (e.g., fcc or ccp).

$$\therefore \text{Number of } \text{Br}^{\ominus} = 4 \text{ (corner + face centre} = 1 + 3 = 4).$$

$$\begin{aligned} \text{Number of alternate OVs} &= 6 \times \frac{1}{4} \text{ (Edge center share)} \\ &= \frac{3}{2} = 1.5 \end{aligned}$$

Number of $\text{Rb}^{\oplus}$ initially = Edge centre + body centre

$$= 12 \times \frac{1}{4} + \frac{1}{1} = 4$$

$$\text{Number of } \text{Rb}^{\oplus} \text{ ion left} = 4 - 1.5 = 2.5$$

Thus, formula is: $\text{Rb}_{2.5}\text{Br}_4$.

121. (4) Fact

122. (3) Fact

123. (2) Density of crystals decrease due to Schottky defects. Effective no. of atoms per unit cell in given lattice

$$= 4 \left(1 - \frac{0.25}{100} \right) = 3.99$$

$$\rho = \frac{50 \times 3.99}{6 \times 10^{23} (0.50 \times 10^{-7})^3}$$

$$\Rightarrow = \frac{50 \times 3.99}{6 \times 125 \times 0.1}$$

$$\rho = 2.66 \text{ g / cm}^3$$

124. (2) The ions leaves its correct lattice site and occupies an interstitial site.

125. (2) Pentavalent impurities in Ge gives *n*-type semiconductors.

126. (4)

127. (3) $2d \sin \theta = n\lambda$ (Bragg's eqn)

$$\text{For } n = 1$$

$$2d \sin \theta = \lambda$$

$$\text{i. If } \theta = 30^\circ \Rightarrow 2d \sin 90^\circ = \lambda$$

$$\therefore d = \lambda$$

$$\text{ii. If } \theta = 90^\circ \Rightarrow 2d \sin 90^\circ = \lambda$$

$$\therefore d = \lambda/2$$

128. (1) Levitation occurs when objects float in air. This can be achieved by mutual repulsion between permanent magnet and a super conductor.

129. (2) The molecules with general formula ABO_3 or ABC_3 posses pervoskite structure.

130. (3) Due to Frenkel defects, density does not change.

131. (2)

132. (2) SiO_2 is used in solar cells.

133. (2) Since equal number of cations ($2 \text{ Na}^{\oplus}$ ions) and anions ($2 \text{ Cl}^{\ominus}$ ions) are missing in the figure given, so it is Schottky defect.

134. (1) *p*-type

135. (3) Electrical conductivity of semiconductors lies in the range 10^{-9} – $10^2 \text{ ohm}^{-1} \text{ cm}^{-1}$.

136. (2)

137. (1)

138. (2)

139. (3) AgBr has Frenkel defects due to large difference in the size of $\text{Ag}^{\oplus}$ and $\text{Br}^{\ominus}$ ions.140. (2) For n -type, impurity added to silicon should have more than 4 valence electrons.

141. (1)

142. (1) Ge is Group 14 elements. Positive holes can be created by adding Group 13 element, i.e., trivalent impurity.

143. (1)

144. (2) See text.

145. (1) Schottky defect is due to missing of equal number of cations and anions from their lattice sites.

146. (2) Frenkel defect is due to missing of anion from its lattice site (causing a vacancy or a hole there) and it occupies the interstitial sites.

147. (2) Same explanation as in Q. 146 above.

148. (2) Because in both types of defects, the electrical conductivity is due to the movement of ions in one direction and movement of hole to other side.

149. (1) Factual statement.

150. (2) Conduction increases due to the movement of ion in one direction and movement of hole on the other direction on applying electric field.

151. (1, 3, 4) All factual statements.

152. (1, 2, 3, 4) All factual statements.

153. (1, 2, 3, 4) All factual statements.

154. (3) Refer to fig. 1.44 (e) and 1.45 (d)

155. (2) In sphalerite (ZnS) = 50% TV (i.e., 4) are occupied
In antifluorite (Na_2O) = cation occupy all T.V (i.e., 8)156. (2) $hcp = AB AB AB \dots$ pattern repeat

For calculating voids between two layers A and B

Total tetrahedral voids = 12 out of which 8 are completely inside but rest are shared by other unit cells.

Total octahedral voids = 6. All are completely inside.

157. (2) Height (c) = $2a \times \sqrt{\frac{2}{3}}$ ($\therefore a = 2r$)

$$\therefore \left(\frac{c}{a}\right) = \frac{4r}{r} \times \sqrt{\frac{2}{3}} = 4 \times \sqrt{\frac{2}{3}}$$

 $\therefore Z_{\text{eff}}$ in $hcp = 6$ 158. (1) In rutile (TiO_2) each Ti^{4+} ion is octahedrally surrounded by six O^{2-} ions whereas each O^{2-} ion is surrounded by only three Ti^{4+} ions, arranged at the three corners of a plane triangle. The C.N. of Ti^{4+} and O^{2-} ion are 6 and 3 respectively.

CN of cation = Number of anions

CN of anion = Number of cations

159. (2) Spinel structure: $\text{A}^{+2} \text{B}_2^{3+} \text{O}_4^{2-}$

$$\text{Number of } \text{A}^{+2} \text{ ions} = \frac{1}{8} \times \text{TV's} = \frac{1}{8} \times 8 = 1$$

(1 T.V is occupied)

$$\text{Number of } \text{B}^{+3} \text{ ions} = \frac{1}{2} \times \text{OV's} = \frac{1}{2} \times 4 = 2$$

(2 OV's are occupied)

$$\text{Number of TV's unoccupied} = 8 - 1 = 7$$

$$\text{Number of OV's unoccupied} = 4 - 2 = 2$$

$$\therefore \left(\frac{\text{TV}}{\text{OV}}\right)_{\text{unoccupied}} = 7 : 2$$

$$\left(\frac{\text{TV}}{\text{OV}}\right)_{\text{occupied}} = 1 : 2$$

160. (3)

$$1. \text{ In CsCl} = \frac{\text{Cs}^{\oplus}}{\text{Cl}^{\ominus}} = \frac{1.69}{1.81} = 0.93$$

(range lies between 0.732 and 1)

$$\therefore \text{CN} = 8$$

$$2. \frac{\text{Mg}^{2+}}{\text{S}^{2-}} = \frac{0.65}{1.84} = 0.35$$

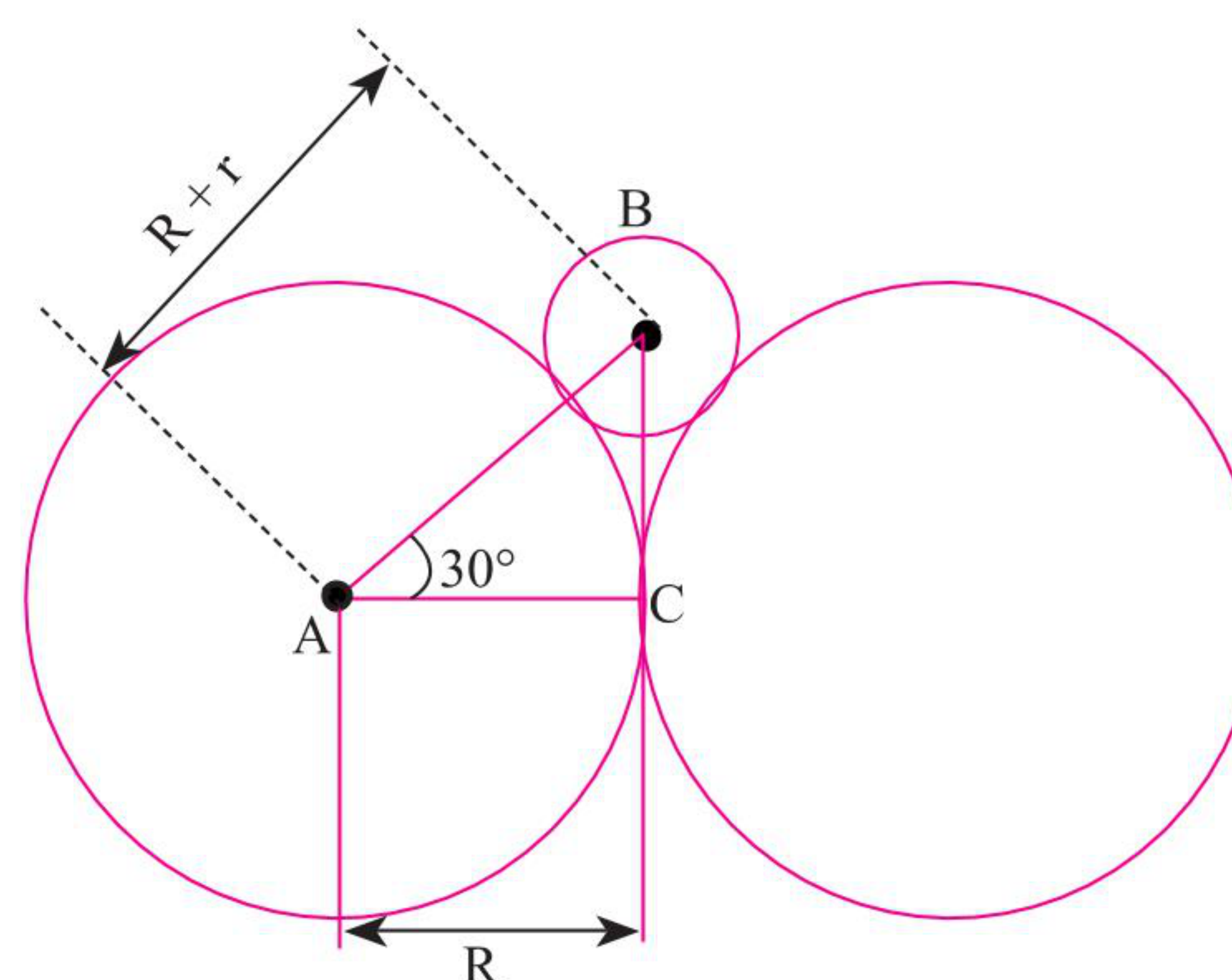
(range lies between 0.225 and 0.414)

$$\therefore \text{CN} = 4$$

$$3. \text{ In MgO: } \frac{\text{Mg}^{2+}}{\text{O}^{2-}} = \frac{0.65}{1.40} = 0.48$$

(Range lies between 0.414 and 0.732)

$$\therefore \text{CN} = 6$$

161. (3) Let R is the radius of larger circle and r is the radius of the triangular hole:

$$\text{In } \triangle ABC, \cos 30^\circ = \frac{\text{Base}}{\text{Hypotenuse}} = \frac{AC}{AB} = \frac{R}{R+r},$$

$$\Rightarrow (R+r) \cos 30^\circ = R.$$

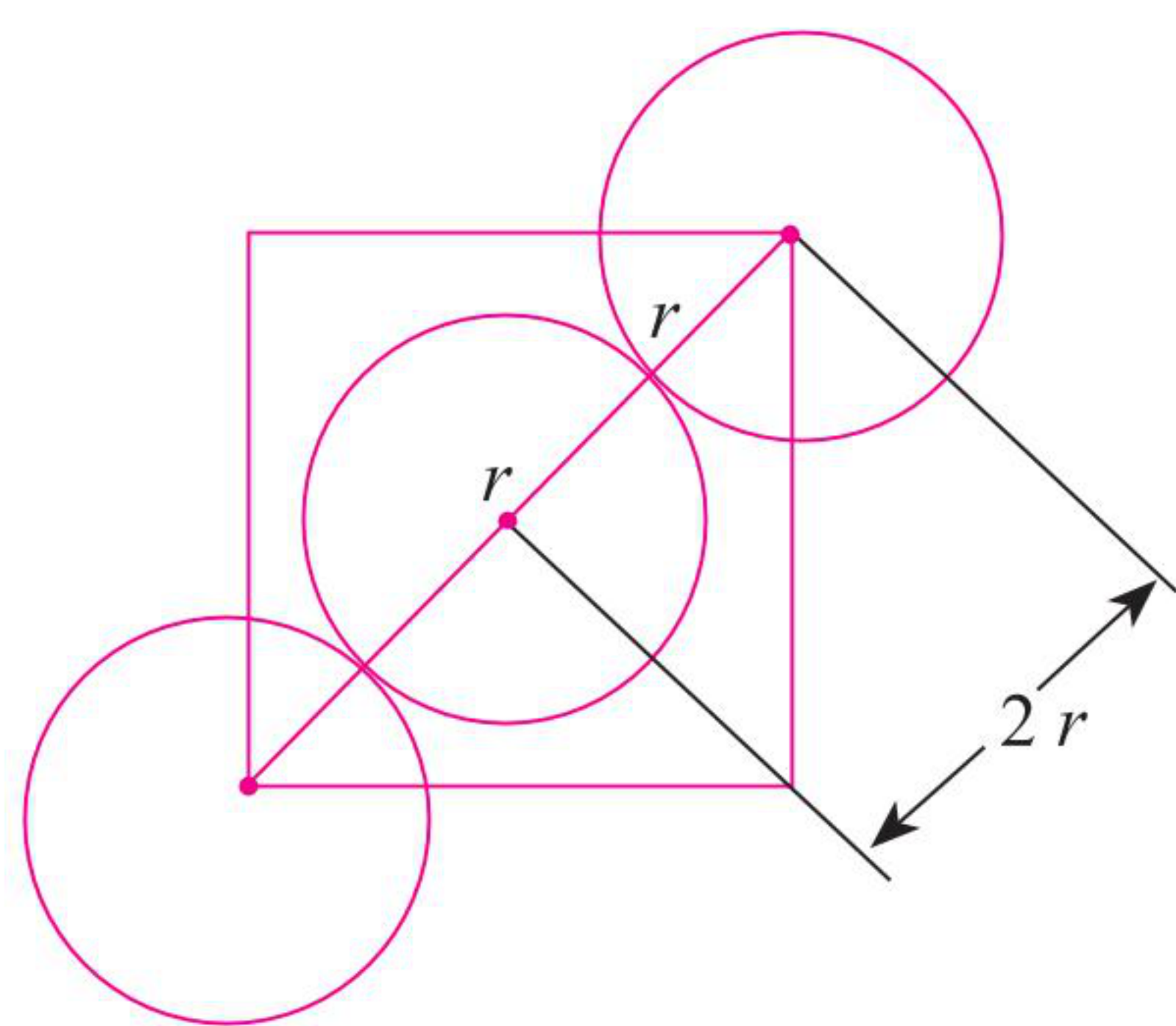
$$\Rightarrow r = \left(\frac{2}{\sqrt{3}} - 1\right)R$$

162. (2) Pentagonal lattice is not possible because the interior angle of a regular pentagonal is 108° which is not an integral factor of 360° 163. (1) In fcc , $Z_{\text{eff}} = 4$.

$$\text{For } fcc, \text{ atomic radius } (r) = \frac{a}{2\sqrt{2}}$$

i. Closest distance between two Au atoms = $2r$

$$= 2 \times \frac{a}{2\sqrt{2}} = \frac{2}{\sqrt{2}} = \frac{4.242}{\sqrt{2}} = \frac{4.242}{1.414} = 3.0 \text{ \AA}$$



ii. Packing factor for fcc lattice = $\frac{\sqrt{2}}{6} \pi = 0.7404$

164. (4) Atom (carbon) lying in the tetrahedral voids touches the surrounding 4 atoms at a distance of $\sqrt{3} \frac{a}{4}$, and the face centre has 12 next nearest neighbours at a distance of $a/\sqrt{2}$

The packing fraction (PF) = $\frac{8 \times \frac{4}{3} \pi R^3}{a^3}$

where $2R = \frac{\sqrt{3}a}{4} \Rightarrow \frac{R}{a} = \frac{\sqrt{3}}{8}$

Hence, PF is: $\frac{32}{3} \pi \left(\frac{3\sqrt{3}}{8 \times 64} \right) = \frac{\sqrt{3}\pi}{16} \approx 0.34$

165. (1) Factual statement

Multiple Correct Answers Type

1. (1, 3)

The hcp and ccp structures have same CN (12), same packing fraction (0.74), but different density as the number of atoms as well as the volume of unit cell differ in both.

2. (1, 4)

On a body diagonal, two corner Cl^- ions and one Na^+ ion in OV (at body centre) are present.

3. (3, 4)

In both fluorite and antifluorite, 100% TVs are occupied and Z_{eff} (number of formula unit) for both is 4.

4. (1, 2, 4)

In square close packing, CN = 4 whereas in hcp, CN (2D) = 6. So, the ratio is 2 : 3.

5. (1, 3)

(1) CN of Zn^{2+} ion in ZnS = 4.

(2) Number of body diagonal planes in a cube = 6.

(3) Formula unit in rock salt structure = 4.

(4) Formula unit in CsCl structure = 1.

6. (2, 4)

An octahedron has 8 faces and 12 edges.

7. (1, 4)

Use any relation:

$$\rho = \frac{Z_{\text{eff}} \times A_w}{N_A \times a^3} \text{ or } \rho = \frac{Z_{\text{eff}} \times A_w \times 1.67 \times 10^{-24} \text{ g}}{a^3}$$

$$\therefore 2.72 \text{ g cm}^{-3} = \frac{Z_{\text{eff}} \times 27 \times 1.67 \times 10^{-24} \text{ g}}{(404 \times 10^{-10})^3 \text{ cm}^3}$$

$$\therefore Z_{\text{eff}} \approx 4$$

(1) $Z_{\text{eff}} = 4$, means fcc structure.

(4) CN of fcc structure = 12

8. (1, 2, 3)

$r_{\oplus}/r_{\ominus} = 0.732, 0.414$, and 0.225 maximum for OV, TV, and triangular void.

9. (1, 2, 3, 4) Refer Section 1.22.

10. (1, 2, 3)

11. (1, 2)

12. (1, 2, 3, 4)

13. (1, 2, 3, 4)

For NaCl , $r_{\oplus}/r_{\ominus} = 0.414 - 0.732$

But radius ratio for LiBr , KCl , RbCl , and BaO are $0.34, 0.38, 0.77$, and 0.83 , respectively, which are not in the range of $0.414 - 0.732$.

14. (2, 3)

$$\frac{r_{\oplus}}{r_{\ominus}} = \sqrt{\frac{3}{2}} - 1 = 0.225$$

Hence, it is the limiting case where cation in the void of fcc structure is not distorted.

Note: A fluorite-type structure has ccp arrangement in which cation (Ca^{2+} ion) forms fcc arrangement with each Ca^{2+} ion surrounded by 8 anions (F^- ions) and each anion (F^- ion) surrounded by 4 cations (Ca^{2+} ion).

So, number of cations surrounding the particular cation = 12. But at the same time 8 anions (present in TVs) touch the particular cation.

15. (1, 3)

$$\frac{r_{\text{Cs}^{\oplus}}}{r_{\text{Be}^{\ominus}}} = \frac{1.69}{1.95} = 0.867 \text{ (bcc structure)}$$

Hence, $\text{Cs}^{\oplus}$ ion lies at the “body centre of cubic void” where CN of $\text{Cs}^{\oplus} = 8$.

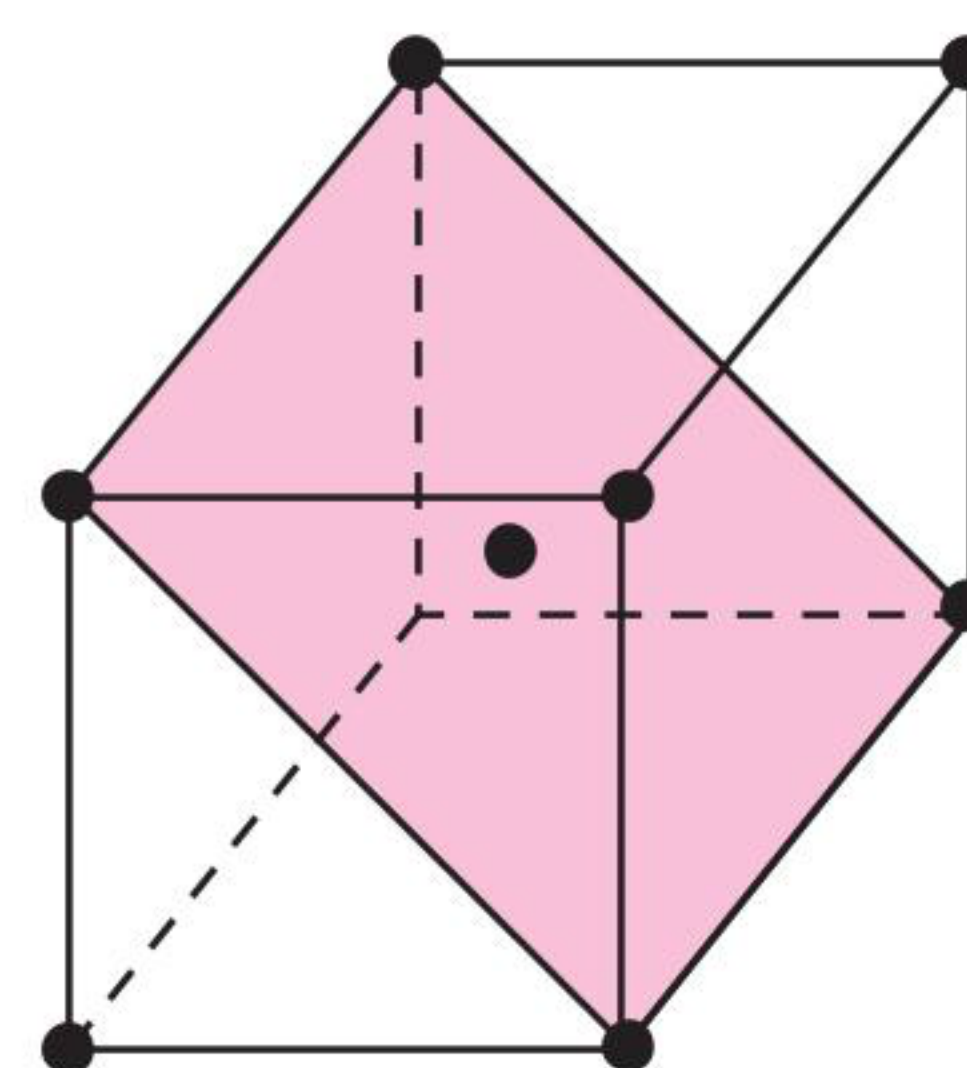
CsBr has bcc structure with $\text{Br}^{\ominus}$ forming simple cubic lattice and $\text{Cs}^{\oplus}$ ion in the void (at body centre).

For bcc,

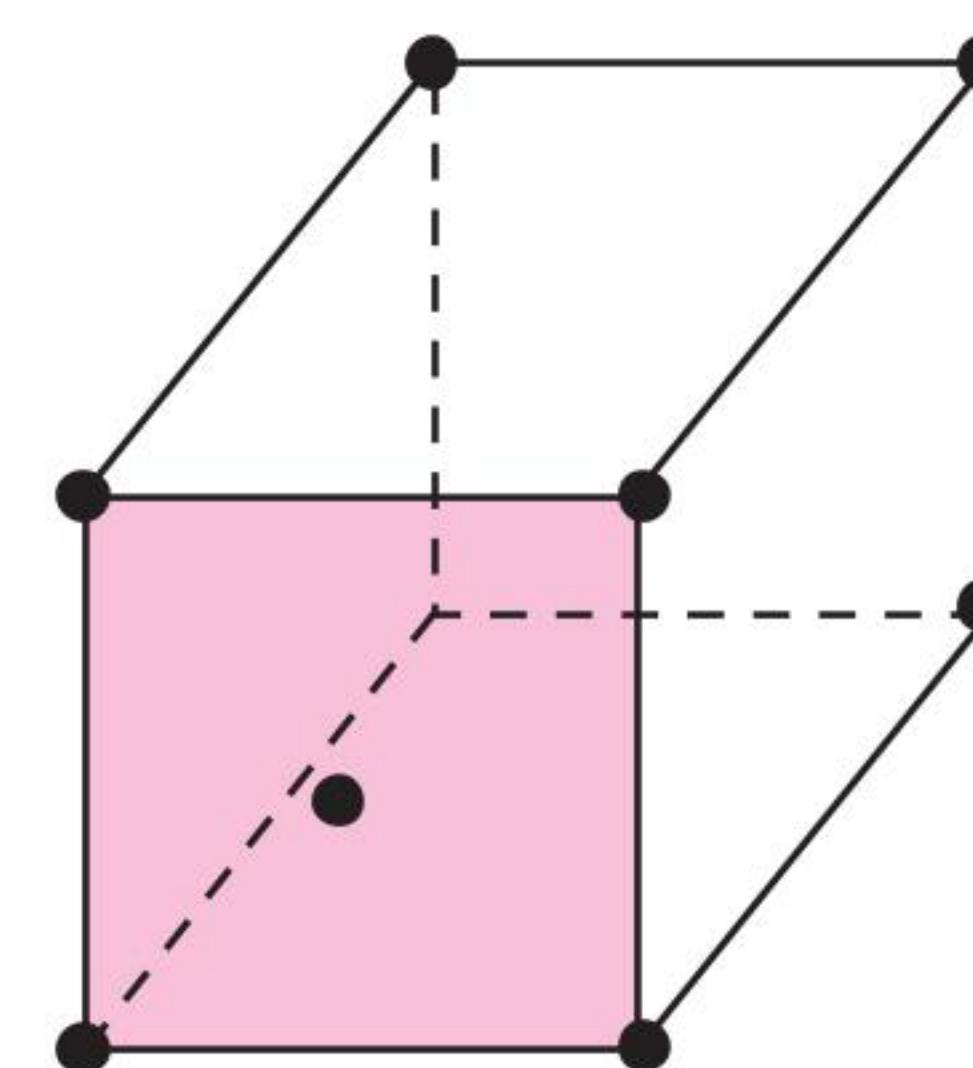
$$2(r_{\text{Cs}^{\oplus}} + r_{\text{Br}^{\ominus}}) = \sqrt{3} a$$

$$2(1.69 + 1.95) = \sqrt{3} a \Rightarrow a = 4.2 \text{ \AA}$$

16. (1, 4)



Body-centered cubic
[Central atom touches other
four atoms in the shaded plane]



Face-centered cubic
[Central atom touches other
four atoms in the shaded plane]

Hence, answer is (1) and (4).

17. (1, 2, 4)

Graphite is a good conductor, sp^2 hybridized, a covalent crystal and crystalline (not amorphous).

18. (1, 2, 4) Factual statement.

19. (1, 2, 3, 4)

$$Z_{\text{eff}} = \frac{\rho \times a^3 \times 10^{-30} \times N_A}{Mw} = \frac{2.75 \times (654)^3 \times 10^{-30} \times 6 \times 10^{23}}{119} = 4$$

 $Z_{\text{eff}} = 4$, suggest fcc structure.

Thus, there are four KBr units. There are 8 ions at the corners and 6 at the face centres.

20. (1, 2, 3)

21. (1, 2, 3)

22. (2, 4)

23. (2)

24. (1, 2, 3, 4)

(A) 2D-hexagonal packing

$$\text{Packing efficiency} = \frac{\pi R^2 + 6 \times \frac{\pi R^2}{3}}{6 \times \frac{\sqrt{3}(2R)^3}{4}}$$

$$\text{(B) Simple cubic} = \frac{1 \times \frac{4}{3} \pi R^3}{a^3}$$

$$a = 2R$$

$$\text{hcp} = (3D) = \frac{6 \times \frac{4}{3} \pi R^3}{24\sqrt{2}R^3}$$

$$\text{fcc} = (3D) = \frac{4 \times \frac{4}{3} \pi R^3}{(2\sqrt{2}R^3)^3}$$

25. (1, 3)

$$\frac{r_{A^{2+}}}{r_{B^{2-}}} = \frac{100}{300} = 0.333 \quad \frac{r_{C^{\oplus}}}{r_{D^{\ominus}}} = \frac{240}{480} = 0.5$$

B^{2-} are at F.C.C lattice point and A^{2+} ions are alternate tetrahedral void

 $D^{\ominus}$ at F.C.C lattice point $C^{\oplus}$ in all octahedral void

C.N. of AB = 4 : 4

C.N. of CD = 6 : 6

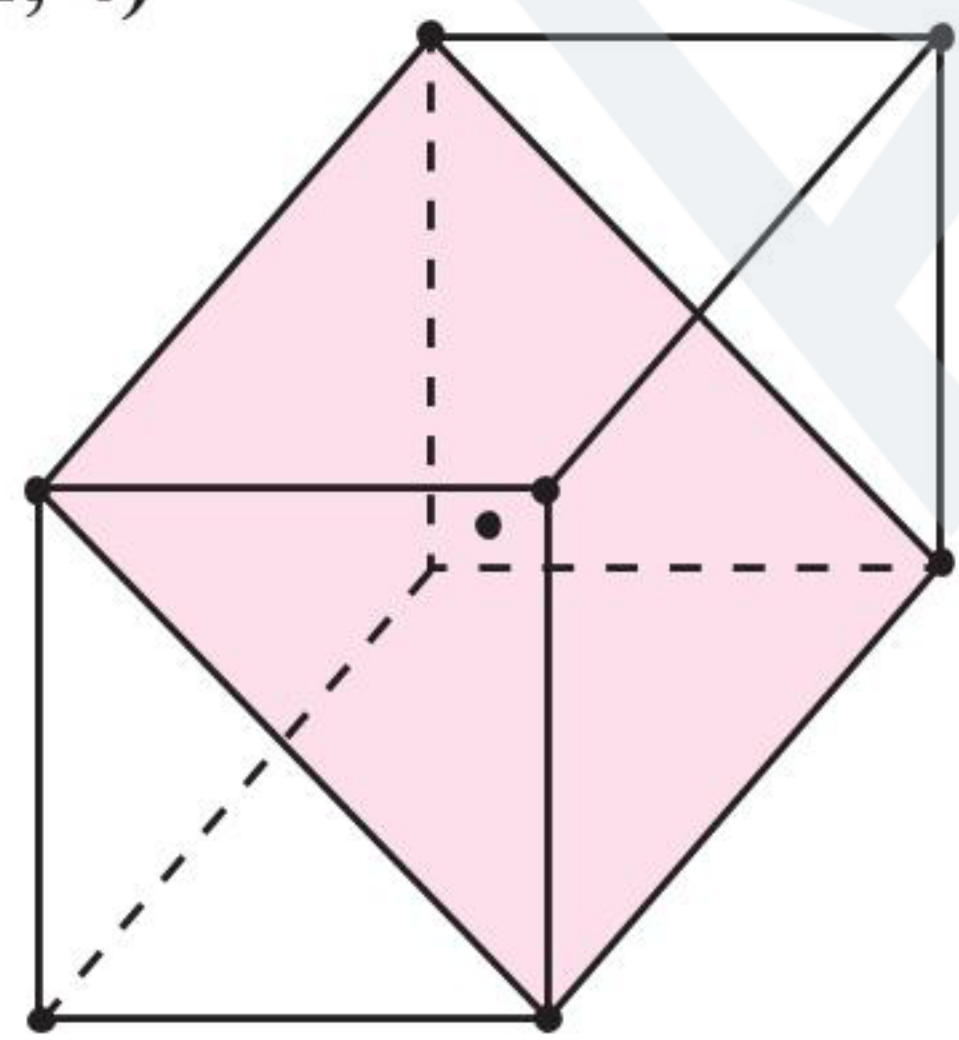
26. (3, 4)

For hexagonal system $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ For triclinic system $\alpha \neq \beta \neq \gamma \neq 90^\circ$

27. (2, 3, 4)

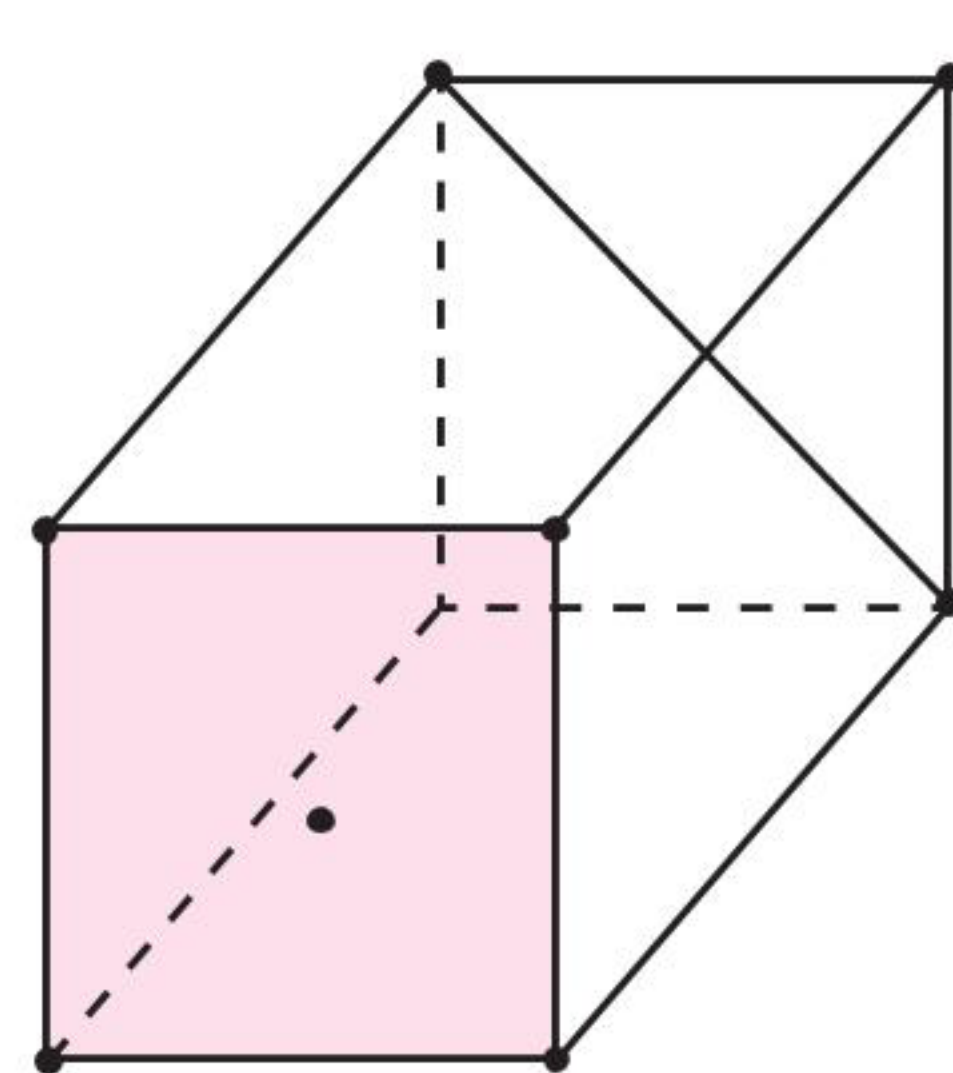
Only (1) is wrong because in tetragonal system, $a = b \neq c$. In all other cases $a \neq b \neq c$.

28. (1, 4)



Body-centered cubic

[Central atom touches other four atoms in the shaded plane]



Face-centered cubic

[Central atom touches other four atoms in the shaded plane]

29. (1, 2, 4)

(1) The body diagonal is $\sqrt{3}$ (5.20 Å) = 9.01 Å. The nearest neighbors along that diagonal are half that distance apart, 4.50 Å

(2) 4.20 Å along the cell edge.

(3) 8 (The body-centre is next to 8 corners.)

(4) 6 (The corner has neighbors along each cell edge: up, down, in, out, left, right.)

30. (2, 3)

OVs are formed at the edge centre and body centre of fcc per unit cell.

31. (1, 3, 4)

For spinel structure, O^{2-} ions form fcc arrangement. $\therefore$ Number of O^{2-} ions = 4,

Number of TV = 8, Number of OV = 4

$$\text{Number of } Mg^{2+} \text{ ions} = \frac{1}{8} \times TV = \frac{1}{8} \times 8 = 1$$

$$\text{Number of } Al^{3+} \text{ ions} = \frac{1}{2} \times OV = \frac{1}{2} \times 4 = 2$$

So, 50% OVs are occupied and 1/8th, i.e., 12.5% TVs are occupied.

32. (1, 2, 3, 4)

(1) P_1 represents one of the close-packed layer having triangular voids only.(2) P_2 contains location of OVs (edge centres of unit cell).(3) P_3 contains 3 OVs locations (one at body centre and two at edge centre). Also, plane P_3 contains the body diagonals, hence it contains TVs location (TVs lie at body diagonal).

33. (1, 2)

OVs are present at edge centres and body centre in an fcc unit cell.

34. (2, 3)

Two TVs are present on each body diagonal of a fcc unit cell at a distance of $\sqrt{3}a/4$ from each corner. (Refer Section 1.14.4, Figs. 1.44(d) and 1.44(e).

35. (1, 2, 3)

Refer Section 1.14.4, Figs. 1.44(d) and 1.44(e).

36. (1, 2, 3, 4)

Refer Section 1.14.4, Figs. 1.44(d) and 1.44(e).

37. (1, 3)

$$\frac{r_{Na^{\oplus}}}{r_{Cl^{\ominus}}} = \frac{95}{181} = 0.52$$

 $Cl^{\ominus}$ ion at fcc lattice point $Na^{\oplus}$ ion are at octahedral void C.N. of NaCl = 6 : 6

$$r_c + r_a = \frac{a}{2}$$

38. (1, 2, 3)

Fact

39. (3, 4)

Tetrahedral voids are formed when the triangular void of the second layer lie exactly above the triangular void in the first layer and the triangular shape of these voids oppositely overlap

40. (2, 3)

Fact

41. (1, 2, 3)

NaCl has 74% of occupied space.

42. (1, 2, 3)

Na_2O has antifluorite structure in which O^{2-} ions are present in ccp while Na^+ ions occupy all the tetrahedral voids which are located at body diagonals.

43. (1, 2, 3, 4)

- (1) NaCl have fcc structure so nearest neighbour distance = $a/2$
 (2) CaF_2 has ccp arrangement in which Ca^{2+} ions form fcc in which each Ca^{2+} ion is surrounded by 8F^- ion and occupy all tetrahedral voids.
 (3) In Na_2O , negative ions form ccp arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion by 8 positive ions. The cations occupy half of the tetrahedral voids. So nearest neighbor distance in CaF_2 and $\text{Na}_2\text{O} = a\sqrt{3}/4$
 (4) CaCl has bcc arrangement so nearest neighbor distance = $a\sqrt{3}/2$

44. (1, 2, 3, 4)

Non-stoichiometric NaCl has F-centres due to anion vacancy defect.

45. (2, 3, 4)

46. (1, 2, 3, 4)

47. (1, 2, 3, 4)

48. (1, 2, 4)

49. (1, 2, 3, 4)

50. (1, 3, 4)

51. (1, 2, 3, 4)

52. (1, 2, 3)

Number of atoms = 4 (for ccp crystal)

Formula = $4\text{AB}_2 = \text{A}_4\text{B}_8$

$\therefore$ CN of A = 8 [CN of A = Number of B atoms]

CN of B = 4 [CN of B = Number of A atoms]

In ccp arrangement, all TVs are occupied (fluorite-type structure).

53. (1, 4)

When KCl crystals are heated it leads to the deposition of potassium ion on surface of KCl. The Cl^- ions diffuse to the surface of crystal and lose electron by potassium atom to form K^+ ion. Released electrons occupies anionic site which is known as F-centre and impart colour to the crystal.

54. (2, 3)

Frenkel defect is present in those compounds which have large difference in the size of cation and anions like ZnS. In Schottky defect the number of ion decreases, density of the solid also decreases.

55. (1, 2, 4)

Excess of Li in LiCl makes it pink

56. (1, 2)

In Frenkel defect as no ions are missing from the crystal as a whole, therefore density of the solid remains unchanged and as similar charges come closer, this result in the increase of dielectric constant of the crystals.

57. (1, 4)

Ferrimagnetic substances lose ferrimagnetism on heating and become paramagnetic. In ferromagnetic substance, domains are aligned in parallel and antiparallel direction in unequal numbers. In ferromagnetic substances, all the domains get oriented in the direction of magnetic field and remain as such even after removing magnetic field.

Hence, (1) and (4) are correct choices.

58. (1, 2, 3)

Gallium acts as a superconductor at 1.1 K.

Linked Comprehension Type

Paragraph 1

1. (1) For fcc,

$$\begin{aligned} \text{Number of } \text{O}^{2-} \text{ ions} &= 8 (\text{corners}) \times \frac{1}{8} \text{ per corner share} \\ &\quad + 6 (\text{faces}) \times \frac{1}{2} \text{ per face share} \\ &= 4 \end{aligned}$$

$$\text{Number of } \text{Si}^{4+} \text{ ions} = \frac{1}{4} \times \text{OV} = \frac{1}{4} \times 4 = 1/\text{unit cell}$$

$$\text{Number of } \text{Fe}^{2+} \text{ ions} = \frac{1}{4} \times \text{TV} = \frac{1}{4} \times 8 = 2/\text{unit cell}$$

$$\begin{aligned} \text{So, formula of "FAYLITE" is } &\text{Fe}_2 \text{Si}^{4+} \text{O}_4^{2-} \\ \Rightarrow &\text{Fe}_2\text{SiO}_4 \end{aligned}$$

2. (3) Number of Na^+ ions in fcc = $\frac{1}{2} \times \text{TV} = \frac{1}{2} \times 8$
 $= 4/\text{unit cell}$

$$\text{So, formula of solid} = \text{Na}_4 \text{Si}^{4+} \text{O}_4^{2-} \Rightarrow \text{Na}_4\text{SiO}_4$$

3. (2) Let the volume of "OLIVINE" unit cell = 100 mL

Volume of unit cell occupied by "fayalite" mineral = x mL

Volume of unit cell occupied by "forsterite" mineral = $(100 - x)$ mL

$$\therefore 3.88 = \frac{x \times 4.34 + (100 - x) \times 3.21}{100}$$

On solving, $x = 59.3$

Paragraph 2

(a) Y^- is smaller than X^- .

The difference in internuclear distance between AX and BX indicates that the cation must not be touching all the anions in AX (smaller cation, larger anion) [see Q.10, Fig. (a)]. There must be anion-anion contact in this compound.

$$\therefore \text{Anion-anion distance} = 2r_-$$

The remaining radius ratio is represented in [see Q.9 Figure].

$$(b) \text{Radius of } \text{X}^- (r_-) = \frac{2.40}{2} = 1.20 \text{ \AA}$$

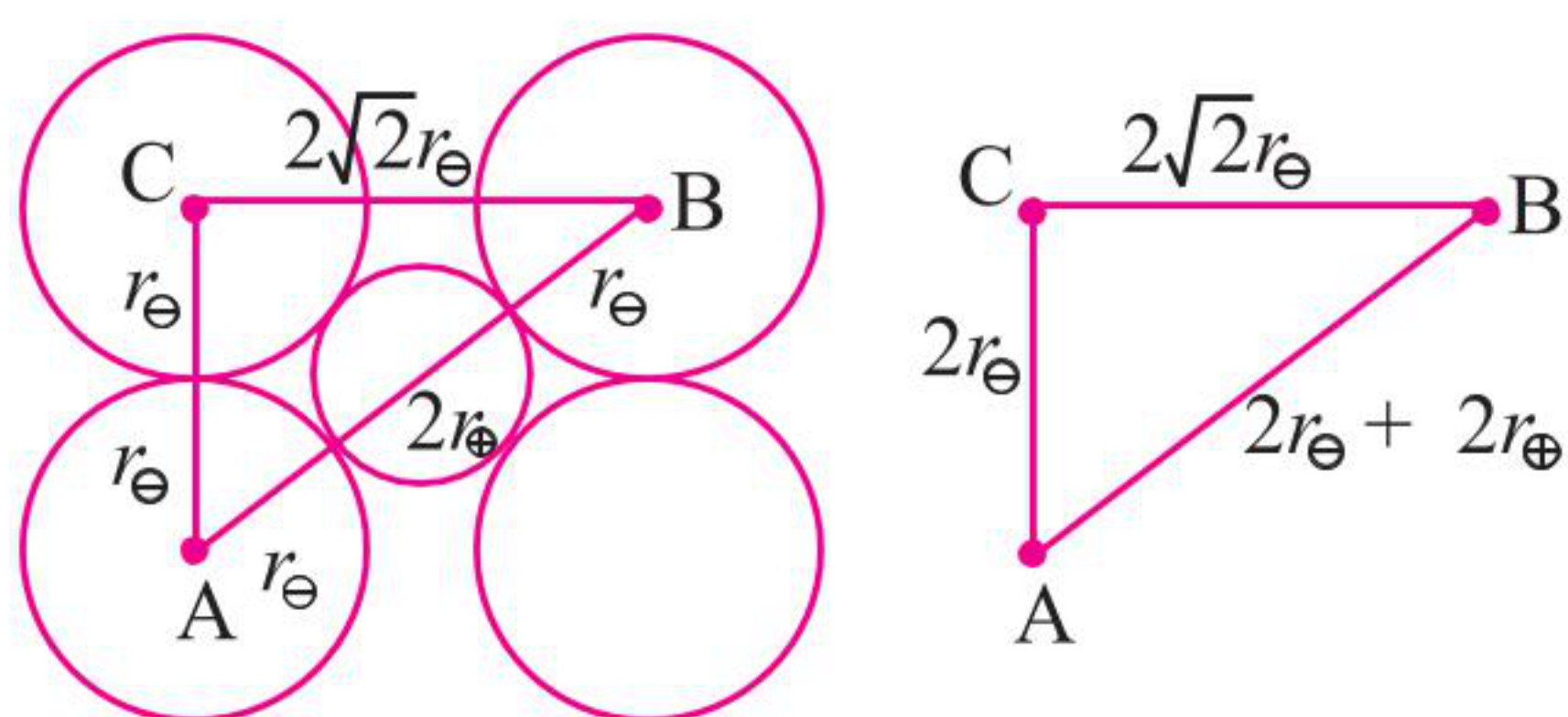
$$\text{Radius of } \text{B}^+ (r_+) = (1.88 - 1.20) \text{ \AA} = 0.68 \text{ \AA}$$

$$(c) \text{Similarly, radius of } \text{Y}^- (r_-) = (1.48 - 0.68) = 0.80 \text{ \AA}$$

$$\text{Radius of } \text{A}^+ (r_+) = (1.15 - 0.80) \text{ \AA} = 0.35 \text{ \AA}$$

Note: Radius of A^+ cannot be calculated from the $\text{A}^+ - \text{X}^-$ distance, since there is no cation-anion contact in AX.

4. (1) Radius of $A^{\oplus}$ and $B^{\oplus}$, respectively, are = 0.35 and 0.68 Å
5. (3) Radius of $X^{\ominus}$ and $Y^{\ominus}$, respectively, are = 1.20 and 0.80 Å
6. (4) As explained above.
7. (1) As explained above.
8. (3)



The distance between opposite corners of the face of a cube with sides $2r_{\ominus}$ (CB) = $2\sqrt{2}r_{\oplus}$

The distance between the centres of touching atoms (AC) = $2r_{\oplus}$

$$\therefore \text{The distance between two opposite anions} = \sqrt{12}r_{\oplus} = (2r_{\oplus} + 2r_{\ominus})$$

$$\therefore \sqrt{12}r_{\oplus} = (2r_{\oplus} + 2r_{\ominus})$$

$$3.46r_{\oplus} = (2r_{\oplus} + 2r_{\ominus})$$

$$1.46r_{\oplus} = 2r_{\oplus} \Rightarrow \frac{r_{\oplus}}{r_{\ominus}} = 0.732$$

Paragraph 3

9. (3) The distance 0.204 nm comes out to be " $a/\sqrt{3}$ " which corresponds to the perpendicular distance between a corner of unit cell and the plane of the three adjacent corners.
10. (1) The distance 0.176 nm is half the unit cell length ($a/2$) which corresponding to the perpendicular distance between the layers of atoms in one face of the unit cell and the center (Fig. I).
11. (2) The distance 0.124 nm corresponds to $\sqrt{2}/4$ times the unit cell dimension, i.e., one-fourth of the distance from one edge of the cell to the opposite edge (Fig. II). The plane intersects the face-centered atoms of the two sides. The plane including the edge atoms is equivalent to the plane across the center of the unit cell.
12. (4) All the data are consistent with an fcc crystal.

Matrix Match Type

1. (a $\rightarrow$ q, r, s) At body diagonal, two corner ions and one OV (at body centre) lies.
(b $\rightarrow$ p, r, s) C_4 axis (tetrad axis) passes through two face-centred ions, body-centred ion (OV).
(c $\rightarrow$ r) Rectangular plane passes through 4 face-centred ions, 4 edge-centred ions, body-centred ion.
2. (a $\rightarrow$ s; b $\rightarrow$ p; c $\rightarrow$ q; d $\rightarrow$ r)
Refer Section 1.27.2 (Schottky Defect and Non-Stoichiometric Defects).
3. (a $\rightarrow$ q; b $\rightarrow$ p; c $\rightarrow$ s; d $\rightarrow$ r; e $\rightarrow$ t)
(a $\rightarrow$ q) Intercepts at x, y, z are 1, 1, ∞ .
So Miller indices = $\frac{1}{1}, \frac{1}{1}, \frac{1}{\infty} = 1, 1, 0$
(b $\rightarrow$ p) Intercepts at x, y, z are = 1, $\infty, 1$
 $\therefore$ Miller indices = $\frac{1}{1}, \frac{1}{\infty}, \frac{1}{1} = 1, 0, 1$

(c $\rightarrow$ s) Intercepts at x, y, z are = -1, $\infty, 1$
 $\therefore$ Miller indices = $-\frac{1}{1}, \frac{1}{\infty}, \frac{1}{1} = \bar{1}, 0, 1$

(d $\rightarrow$ r) Intercepts at x, y, z are = $\infty, \frac{1}{2}, \frac{1}{2}$
 $\therefore$ Miller indices = $\frac{1}{\infty}, \frac{1}{1/2}, \frac{1}{1/2} = (0, 2, 2)$

(e $\rightarrow$ t) Intercepts at x, y, z are = $\frac{1}{2}, \frac{1}{2}, \infty$
 $\therefore$ Miller indices = $\frac{1}{1/2}, \frac{1}{1/2}, \frac{1}{\infty} = 2, 2, 0$

4. (a $\rightarrow$ q; b $\rightarrow$ r; c $\rightarrow$ p; d $\rightarrow$ s; e $\rightarrow$ t)

(Refer text)

5. (a $\rightarrow$ r; b $\rightarrow$ p; c $\rightarrow$ s; d $\rightarrow$ q; e $\rightarrow$ u; f $\rightarrow$ t)

(Refer text)

6. (a $\rightarrow$ q; b $\rightarrow$ r; c $\rightarrow$ p; d $\rightarrow$ u; e $\rightarrow$ s; f $\rightarrow$ t)

(Refer Table 1.12)

[For (e), refer Section 1.18]

[For (f), refer Section 1.19]

7. (1)

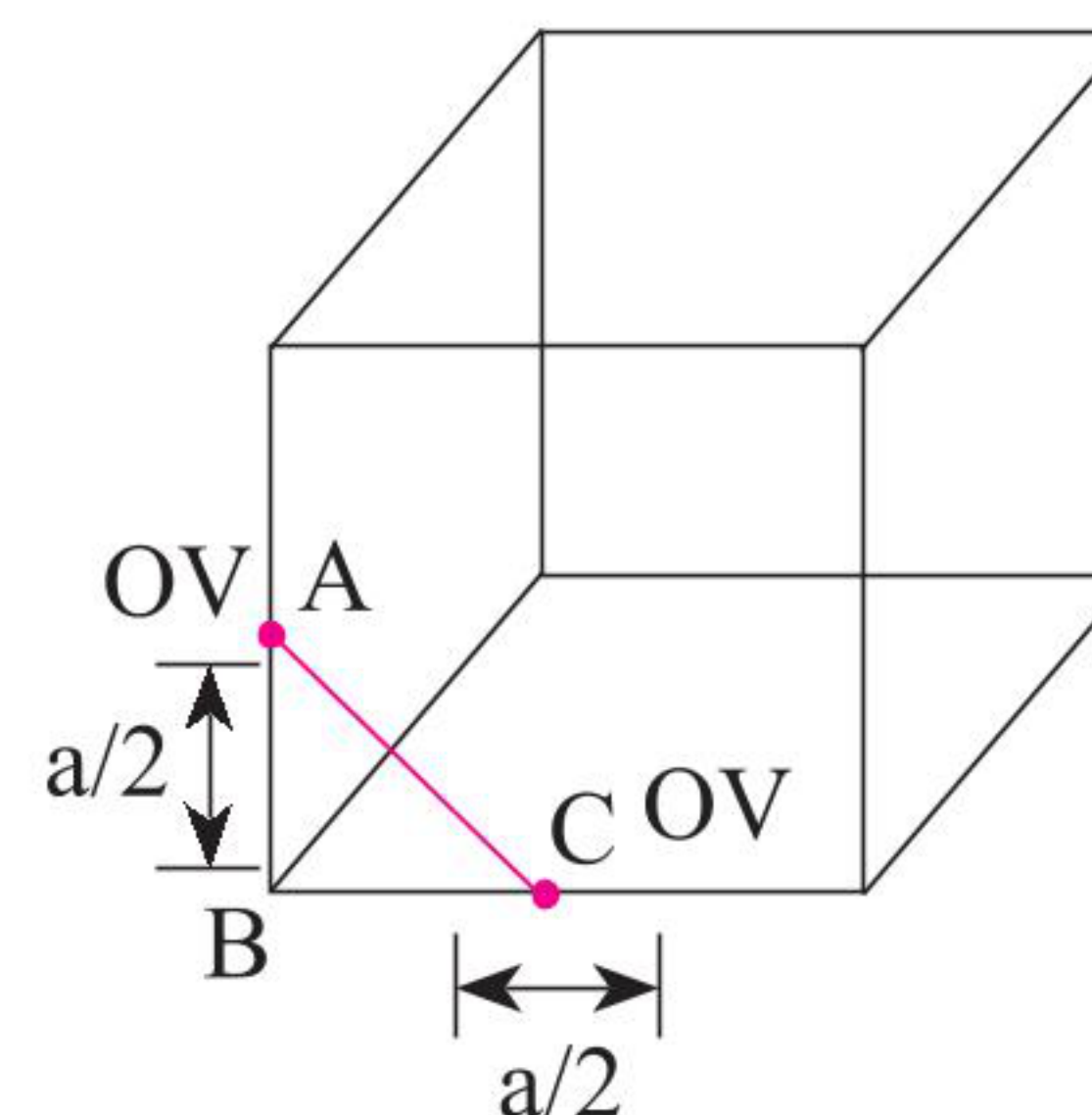
8. (4)

9. (2)

10. (4)

Explanation

7. Refer to section 1.14.4 page 1.32 Physical Chemistry Part - 2
8. Nearest distance between 2 O.V.



$$(AC)^2 = (AB)^2 + (BC)^2 = \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 = \frac{a^2}{2}$$

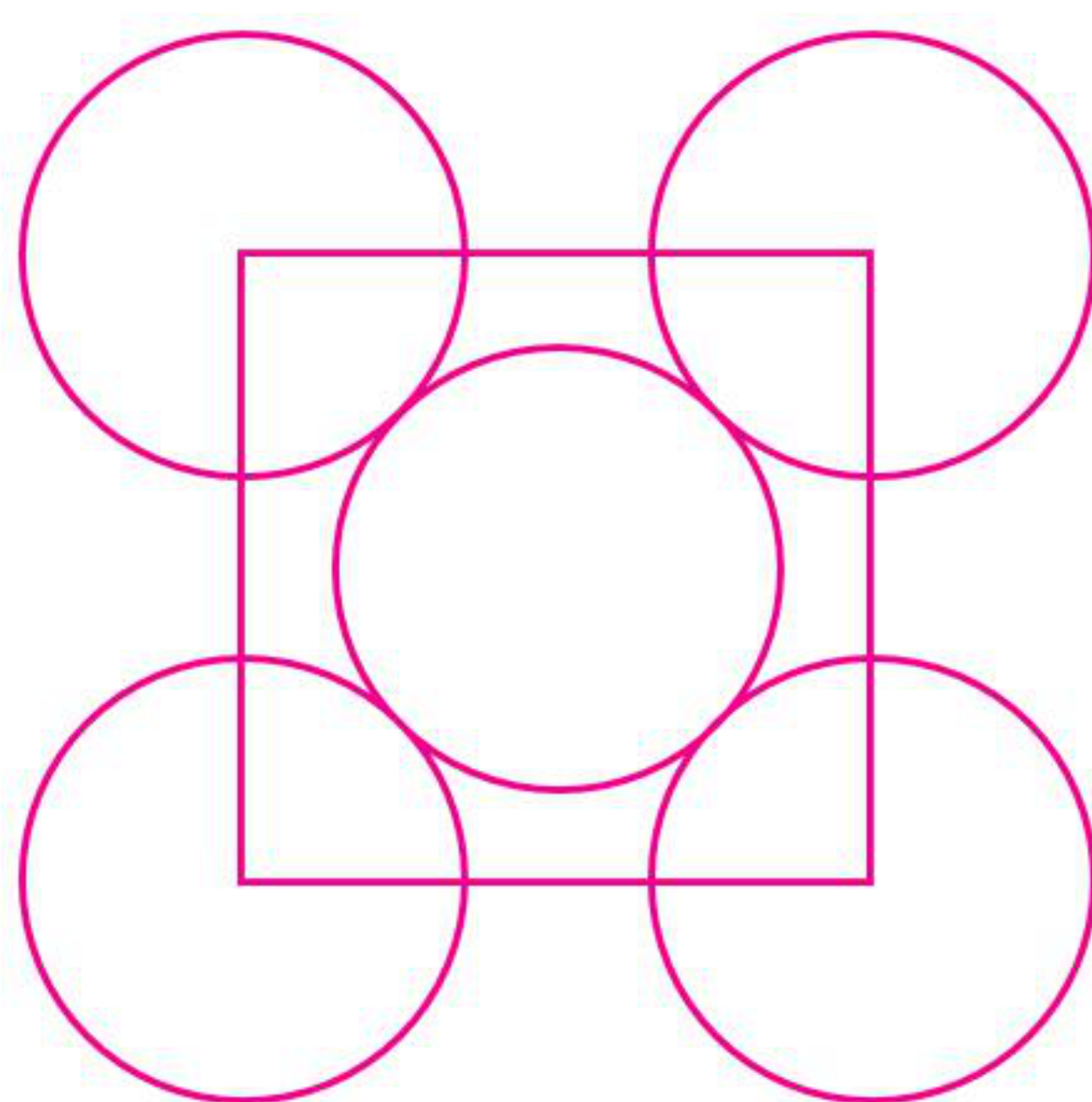
$$AC = \frac{a}{\sqrt{2}}$$

9. Refer to section 1.17 page 1.42 and illustration 1.53 page 1.54 Physical Chemistry Part - 2
10. Refer to table 1.12 page 1.41 Physical Chemistry Part - 2

Numerical Value Type

1. (7) For ZnS structure, (Z_{eff} of ZnS = 4)
Number of $B^{\ominus}$ = 4/unit cell (corner + face centre)
Number of $A^{\oplus}$ = 4/unit cell (in alternate TVs)
Number of $B^{\ominus}$ ion removed = 4 (Two from each face centre)
 $\times \frac{1}{2}$ (per face center share) = 2
Number of $Br^{\ominus}$ ions left = $4 - 2 = 2$ /unit cell
Number of Z^{2+} ions entering in place of $B^{\ominus} = 1$.
[To maintain electrical neutrality, $2 B^{\ominus} = 1 Z^{2+}$]
Formula = $A_4B_2Z_1$
 $\therefore x + y + c = 4 + 2 + 1 = 7$

2. (2) Consider one face of unit cell as shown below.



Number of atoms on one face

$$= 4 (\text{corners}) \times \frac{1}{8} (\text{per corner share}) + 1 (\text{face centre}) \times \frac{1}{2} (\text{face centre share})$$

$$= \frac{1}{2} + \frac{1}{2} = 1/\text{per face}$$

Given number of atoms on all faces = 6×10^{30}

$$\text{Given number of atoms on one face} = \frac{1}{6} \times 6 \times 10^{30} = 10^{30} \text{ atoms}$$

Number of unit cells at one face of crystal

$$= \frac{6 \times 10^{30}}{6} = 10^{30}$$

$$\text{So, number of unit cells at the edge of crystal} = \sqrt{10^{30}} = 10^{15}$$

$$\text{Now, edge length of unit cell} = \frac{4}{\sqrt{2}} \times 50 \text{ nm}$$

$$\text{Edge length of cubical crystal} = \frac{4}{\sqrt{2}} \times 50 \times 10^{15} \text{ nm}$$

$$\begin{aligned} \text{So, area of face of crystal} &= \left(\frac{4}{\sqrt{2}} \times 50 \times 10^{15} \right)^2 \text{ nm}^2 \\ &= \frac{16}{2} \times 25 \times 10^2 \times 10^{30} \\ &= 2 \times 10^{34} \text{ nm}^2 \\ &= 2 \times 10^{-18+34} \text{ m}^2 \\ &= 2 \times 10^{16} \text{ m}^2 \end{aligned}$$

$$\therefore A \times 10^{16} \text{ m}^2 = 2 \times 10^{16} \text{ m}^2$$

$$A = 2$$

3. (2) (Refer Section 1.24.7)

Void volume = 0.22/unit volume of unit cell

$$0.11A = 0.22 \Rightarrow A = 2$$

4. (4) Na_2O has fcc structure.

$$\therefore Z_{\text{eff}} = 4/\text{unit cell}$$

$$\therefore \text{Formula} = 4\text{Na}_2\text{O} = \text{N}_8\text{O}_4$$

$$\therefore \text{Coordination number of Na}^{\oplus} = 4$$

Note: CN of cation = Number of anions

CN of anion = Number of cations

Antifluorite-type structures have (4 : 8) CN and $\text{Na}^{\oplus}$ ions are in all TVs.

5. (7) Let radius of hollow sphere B = r

$$\therefore \text{Edge length } (a) = 4r/\sqrt{3}$$

$$\text{Volume of unit cell} = a^3 = (4r/\sqrt{3})^3$$

Volume of B unoccupied by A (having radius = $r/2$) in unit

$$\text{cell} = 2 \times \left[\frac{4}{3} \pi r^3 - \frac{4}{3} \pi \left(\frac{r}{2} \right)^3 \right]$$

$$\therefore \frac{\text{Volume of B unoccupied by A in unit cell}}{\text{Volume of unit cell}} = \frac{\frac{4}{3} \pi \times \frac{7r^3}{8} \times 2}{\left(\frac{4r}{\sqrt{3}} \right)^3}$$

$$= \frac{7\pi\sqrt{3}}{64}$$

$$\therefore A \times \frac{7\pi\sqrt{3}}{64} = \frac{7\pi\sqrt{3}}{64}$$

$$\therefore A = 7$$

6. (6) Statements (a), (b), and (c) are correct.

So total score = $1 + 2 + 3 = 6$

Statement (a, b) are factual.

$$\text{Statement (c): } \frac{r_{\oplus}}{r_{\ominus}} = \frac{0.35}{0.95} = 0.368$$

The radius ratio lies in the range of 0.225–0.414, which corresponds to TV and the CN of TV = 4.

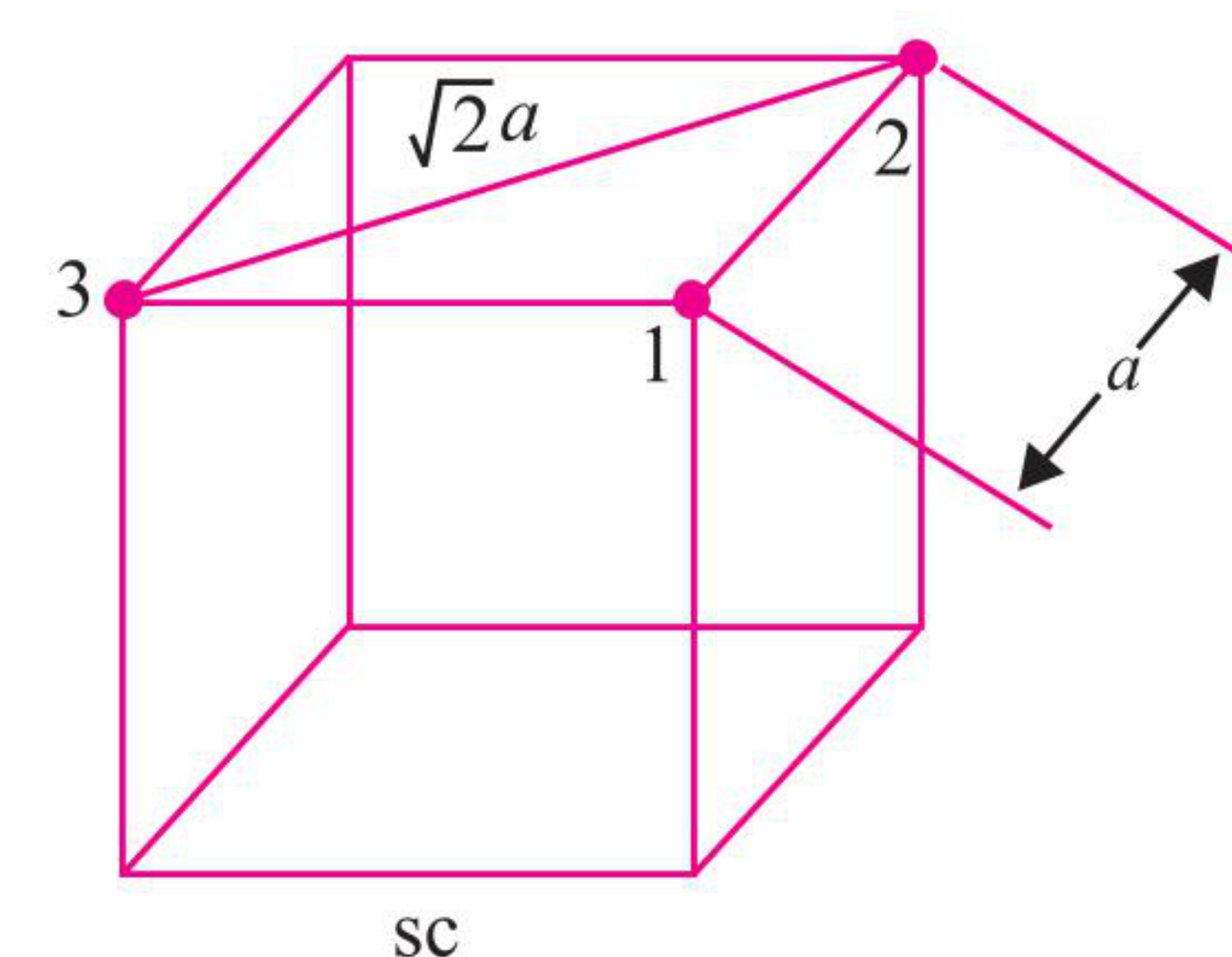
7. (8) Statements (a), (b), and (d) are correct.

(a) So total score = $4 + 3 + 1 = 8$

Nearest neighbour of atom 2 are 1 and 3.

Distance between atoms 1 and 2 = a

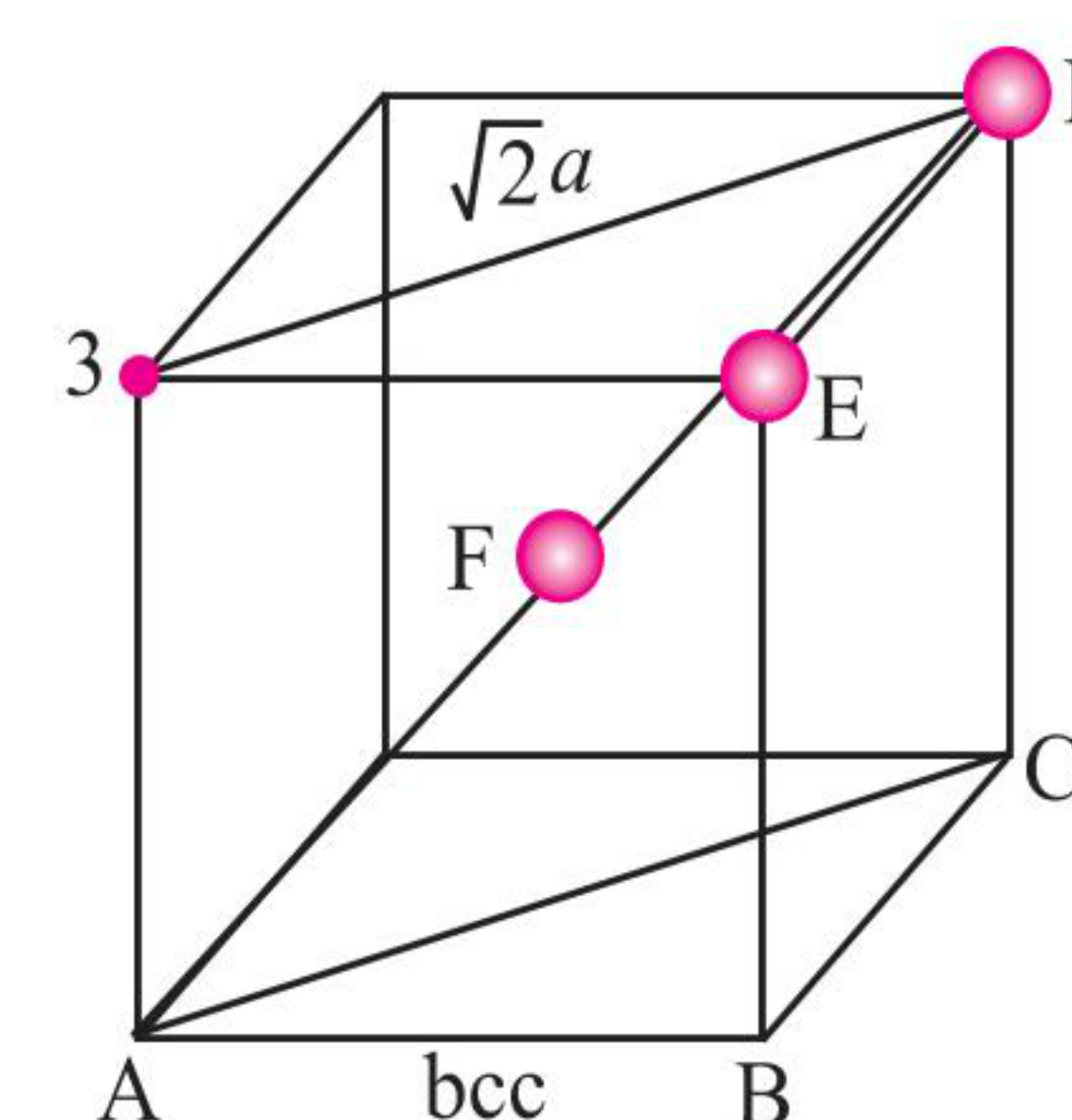
Distance between atoms 2 and 3 = $\sqrt{2}a$



(b) Nearest neighbours of atom D are E and F (F atom is in body centre)

$$\text{Body diagonal (AD)} = \frac{\sqrt{3}}{4} a$$

$$\text{Distance DF} = \frac{1}{2} (\text{AD}) = \frac{\sqrt{3}}{2} a$$



Distance ED = a .

(c) Option (c) is wrong. ZnS (wurtzite) and ZnS (zinc blende) are polymorphs. (Refer Section 1.26). Same substance occurring in different crystal forms is called polymorphism.

But in both the compounds, cations (Zn^{2+} ions) occupy alternate TVs.

In both compounds, S^{2-} occupies lattice points.

(d) Correct statement.

8. (2) Figures A and D. (Refer illustration 1.9)

9. (8) Diameter of Cs = $2 \times 2.6 = 5.2 \text{ \AA} = 5.2 \times 10^{-8} \text{ cm}$

$$\begin{aligned} \text{Number of atoms in } 2.50 \text{ cm row} &= \frac{2.50}{5.2 \times 10^{-8}} \\ &= 0.48 \times 10^8 \\ &= 4.8 \times 10^7 \text{ Cs atoms} \end{aligned}$$

$$\begin{aligned} \therefore \text{Moles of Cs atoms} &= \frac{4.8 \times 10^7}{6 \times 10^{23}} = 0.8 \times 10^{-16} \\ &= 8 \times 10^{-17}. \end{aligned}$$

$$\therefore x \times 10^{-17} = 8 \times 10^{-17}$$

$$\Rightarrow x = 8$$

10. (13) Single unit cell consists of three cubes.

Number of Ba^{2+} ions = 2 per unit cell

Number of Y^{4+} ions = 1 per unit cell

Number of Cu^{2+} ions = 8 in each cube at corners)

$$= 8 \times 3 \text{ (in three cubes)}$$

$$\times \frac{1}{8} \text{ (per corner share)}$$

$$= 3/\text{unit cell}$$

Number of O^{2-} ions = 10 (at edge centre of cube 1)

+ 8 (at edge centre of cube 2)

+ 10 (at edge centre of cube 3)

= 28 (edge centre)

$$\times \frac{1}{4} \text{ (per edge centre share)}$$

$$= 7/\text{unit cell}$$

Formula: $\text{Y}_{(a)}^{4+} \text{Ba}_{(b)}^{2+} \text{Cu}_{(c)}^{2+} \text{O}_{(d)}^{2-}$

$$\Rightarrow \text{Y}_1^{4+} \text{Ba}_2^{2+} \text{Cu}_3^{2+} \text{O}_7^{2-} \quad \left[\begin{array}{l} \text{Total +ve charge (14)} \\ \text{is equal to total -ve} \\ \text{charge (14)} \end{array} \right]$$

$$\therefore a + b + c + d = 1 + 2 + 3 + 7 = 13$$

11. (4) (a) Number of X atoms = $8 \times \frac{1}{8} = 1/\text{unit cell}$.

Number of Y atoms = 1/unit cell

$$\text{Number of O atoms} = 12 \times \frac{1}{4} = 3/\text{unit cell}$$

Formula is: $\text{XYO}_3 \Rightarrow \text{X}_a \text{Y}_b \text{O}_c$

(b) Number of O atoms missing from two edge centres per

$$\text{unit cell} = 2 \times \frac{1}{4} = \frac{1}{2}/\text{unit cell}$$

$$\text{Number of O atoms left} = 3 - \frac{1}{2} = 2.5/\text{unit cell}$$

$$\text{Formula is } \text{XYO}_{2.5} \Rightarrow \text{X}_2 \text{Y}_2 \text{O}_5 \Rightarrow \text{X}_x \text{Y}_y \text{O}_z$$

$\therefore$ The value of

$$(x + y + z) - (a + b + c) = (2 + 2 + 5) - (1 + 1 + 3) = 4$$

Archives

JEE Advanced

Single Correct Answer Type

1. (4) Diagonal = $4r$

$$\text{Diagonal} = \sqrt{L^2 + L^2} = \sqrt{2}L$$

$$\text{or } 4r = \sqrt{2}L$$

$$\text{or } L = \frac{4r}{\sqrt{2}}$$

$$\text{Total area} = L^2$$

$$\text{or } \left(\frac{4r}{\sqrt{2}} \right)^2 \Rightarrow 8r^2$$

Number of spheres inside the square is

$$1 + 4 \left(\frac{1}{4} \right) = 2$$

Area of each sphere = πr^2

Total area of spheres = $2 \times \pi r^2$

$$\text{Packing fraction} = \frac{\text{Total area of spheres}}{\text{Total area}}$$

$$= \frac{2 \times \pi r^2}{8r^2} = \frac{\pi}{4} \approx 0.785$$

2. (2) Number of M atoms = $\frac{1}{4} \times 4 + 1 = 1 + 1 = 2$

$$\text{Number of X atoms} = \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 3 + 1 = 4$$

So, formula of compound is $\text{M}_2\text{X}_4 = \text{MX}_2$

3. (1) Metal oxide = $\text{M}_{0.98}\text{O}$

If 'x' ions of M are in +3 state, then

$$3x + (0.98 - x) \times 2 = 2$$

$$x = 0.04$$

So, the percentage of metal in +3 state would be

$$\frac{0.04}{0.98} \times 100 = 4.08\%.$$

4. (1) No. of oxygen atoms per unit cell in ccp = 4 (O^{2-})

No. of octahedral voids per unit cell = 4 (Al^{+3})

No. of tetrahedral voids per unit cell = 8 (Mg^{+2})

Total negative charge due to oxygen atoms = 8

Net charge must be zero.

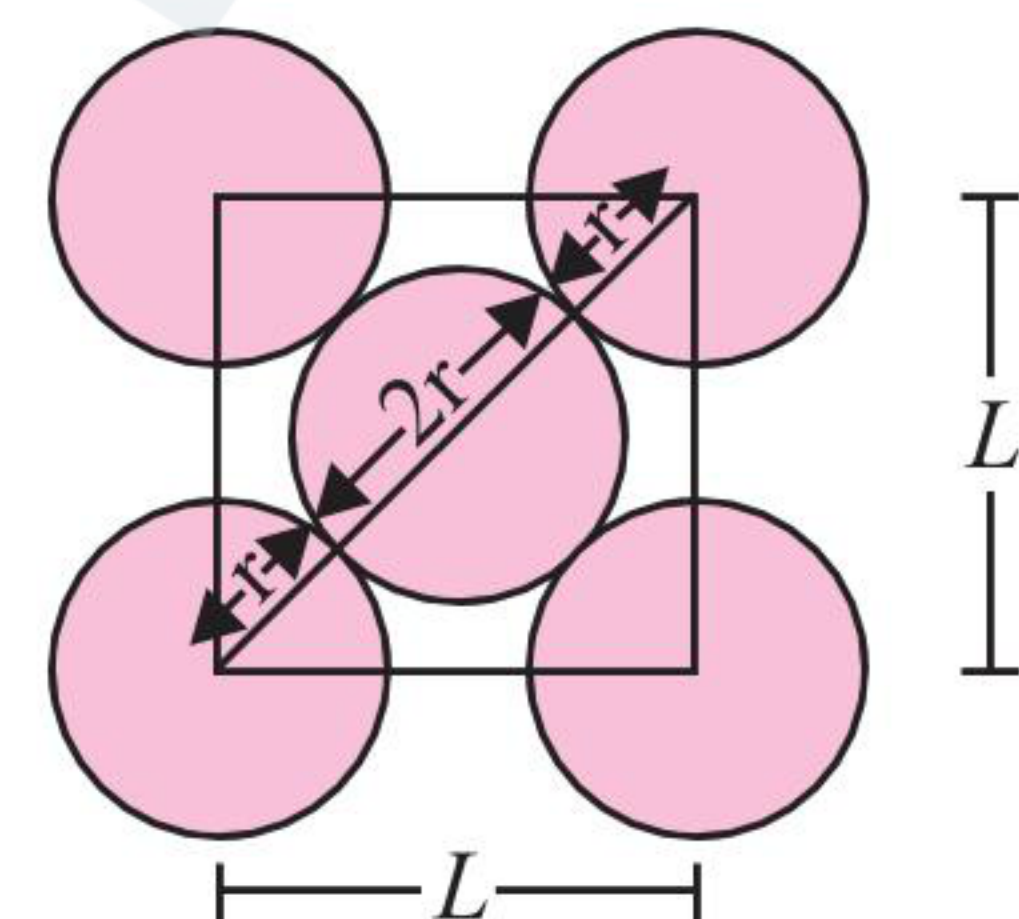
$$m4(3) + 2n(8) + 4(-2) = 0$$

$$3m + 4n = 2$$

$$(1) \quad \frac{3}{2} + \frac{4}{8} = 2 \text{ is correct.}$$

$$(2) \quad 3 \times 1 + 4 \times \frac{1}{4} = 4 \neq 2 \text{ is incorrect.}$$

$$(3) \quad 3 \times \frac{1}{2} + 4 \times \frac{1}{2} = \frac{7}{2} \neq 2 \text{ is incorrect.}$$



$$(4) \quad 3 \times \frac{1}{4} + 4 \times \frac{1}{8} = \frac{3}{4} + \frac{2}{4} = \frac{5}{4} \neq 2 \text{ is incorrect.}$$

$$5. (2) \quad 2[r_x + r_y] = \sqrt{2}a \quad \{a = 2r_y; r_y = 0.59\}$$

$$2[r_x + r_y] = \sqrt{2}(2r_y)$$

$$2r_x = 2\sqrt{2}r_y - 2r_y$$

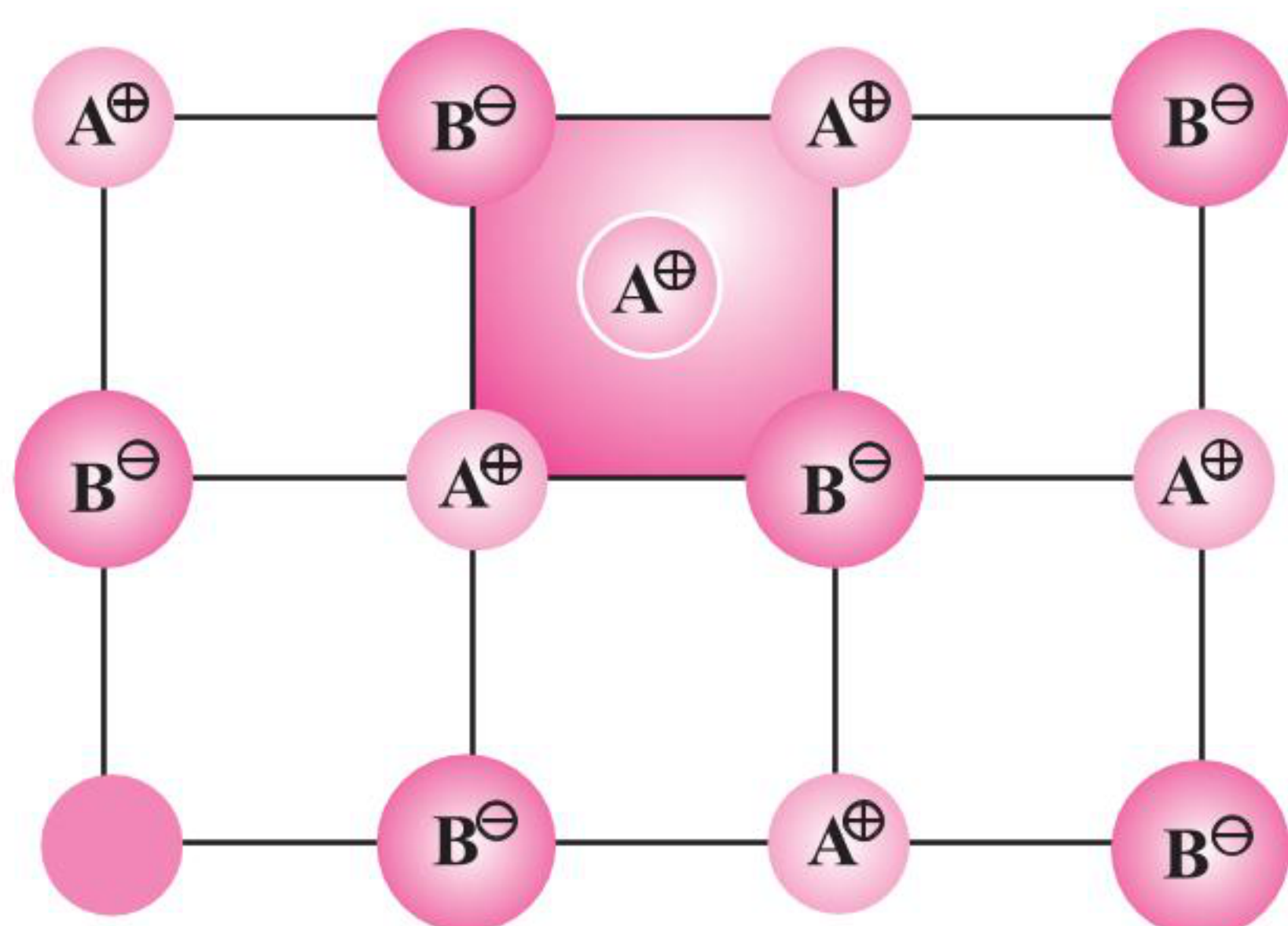
$$r_x = r_y[\sqrt{2} - 1]$$

$$r_x = 0.414r_y = 0.207a$$

$$\text{Packing fraction} = \frac{3 \times \frac{4}{3}\pi r_x^3 + \frac{4}{3}\pi r_y^3}{a^3} = \frac{4\pi(0.207a)^3 + \frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3} = 0.63$$

Multiple Correct Answers Type

1. (2, 3)



In Frenkel defect, certain ions, mostly cations, are missing from their lattice points and are present in the interstitial spaces. (Cations due to smaller size have more chances of slipping.) Stoichiometry is maintained.

In metal excess defects caused by anion vacancies, one or more anions are missing from the lattice points which are occupied by electrons.

The overall electrical neutrality is maintained. When NaCl crystal is heated with Na vapours, this kind of defect is observed.

The electrons impart colour to the crystal (yellow colour to NaCl). These are known as F-centres (Farbe's centres).

2. (2, 3, 4) Factual

The middle layers will have 12 nearest neighbours. The topmost layer will have 9 nearest neighbours.

$4r = a\sqrt{2}$, where ' a ' is edge length of unit cell and ' r ' is radius of atom

3. (1, 3)

(1) (i) Two M cations are at the face centre of the cube.

$$\therefore \text{No. of effective } M \text{ cations} = \left(\frac{1}{2} \times 2\right) = 1.$$

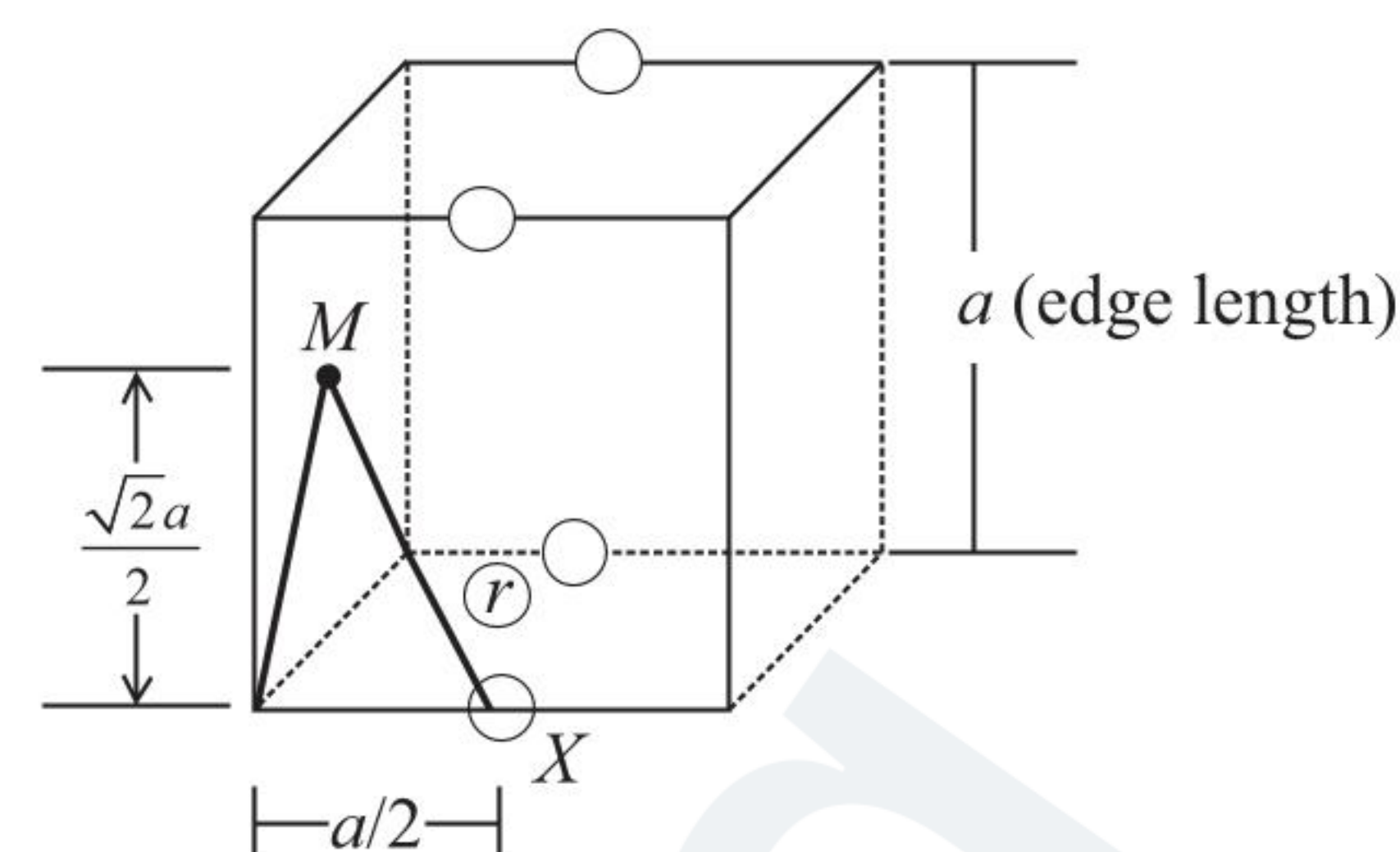
(ii) Four X anions are at the edge centre of the cube.

$$\therefore \text{No. of effective } X \text{ anions} = \left(\frac{1}{4} \times 4\right) = 1$$

Formula of solid = MX .

Statement (2) is wrong. Correct (2) is:

(2) Coordination number of both M and $X = 8$.



Let $M-X$ bond length = r .

$$\therefore r^2 = \left(\frac{\sqrt{2}a}{2}\right)^2 + \left(\frac{a}{2}\right)^2$$

On solving, we get,

$$r = \frac{\sqrt{3}a}{2}.$$

$\therefore$ Ratio of $M-X$ bond length (i.e., r) and unit cell edge length (i.e., a) is:

$$\frac{r}{a} = \frac{\sqrt{3}a}{2a} = \frac{\sqrt{3}}{2} = 0.866$$

Statement (4) is wrong. Correct (4) is:

(4) Compounds in which coordination number of both cations and anions is equal to 8, the radius ratio is:

$$\frac{r_c}{r_a} = 0.732 - 1.$$

Numerical Value Type

1. (8)

Chip all the corners to get truncated octahedral. Each chipped face will be a hexagon.

$$2. (2) \quad d = \frac{Z_{\text{eff}} \times M_w}{N_A \times a^3} \quad (\text{For fcc, } Z_{\text{eff}} = 4)$$

$$8 = \frac{4 \times M_w}{6.022 \times 10^{23} \times (400 \times 10^{-10})^3}$$

$$M_w = 76.8 \text{ g mol}^{-1}$$

$$76.8 \text{ g contain} = 6 \times 10^{23} \text{ atoms}$$

$$\therefore 256 \text{ g will contain} = 20 \times 10^{23} \text{ atoms}$$

$$= 2 \times 10^{24} \text{ atoms}$$

$$\therefore N = 2$$

3. (3) X^- = Octahedral void

M^+ = FC point

M^+ X^-

$$(i) \quad 4 \qquad 4 - 3 = 1$$

$$(ii) \quad 4 - 6 \times \frac{1}{2} \qquad 1 + 6 \times \frac{1}{2}$$

$$(iii) \quad 1 - 1 \qquad 3 + 1 = 4$$

$$(iv) \quad 0 + 1 \qquad 4 - 1 = 3$$

$$\text{Hence } \frac{\text{anion}}{\text{cation}} = \frac{3}{1} = 3$$